ANALYTICAL METHODS

Ingles

MANUAL OF ANALYTICAL METHODS FOR THE URANIUM CONCENTRATING PLANT

by J. C. Ingles

MINES BRANCH
Department of Mines
and Technical Surveys
Ottawa, Canada.

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Radioactivity Division

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Instructions for the Use of this Manual

The Manual consists of three parts:

PART I, General Considerations, provides background information necessary for the efficient application of the analytical methods given in Parts II and III. It is intended as a permanent reference for such matters, and is not likely to be added to or changed.

PART II, Methods, Uranium and Thorium, deals with the elements of major interest, uranium and thorium.

PART III, Methods, Supplementary, is concerned with supplementary methods required in process control and ore analysis.

Each of the three Parts has its own table of contents.

All methods are coded. For example, "The Iodometric Determination of Lead as Chromate" is coded "Pb-1" and each page of the description of the method is marked with this code number. Thus, to find the description in the Manual, it is necessary to determine the code number by consulting the contents pages of the supplementary methods section (Part III) for "Lead"; select this determination, note the code number and then leaf through Part III for "Pb-1". Code numbers are arranged alphabetically, and tabs such as "A to B", "C", "F to M", etc., are used to help locate the code number.

The Division is continually improving and simplifying these methods as well as developing new ones, and from time to time it will be necessary to replace existing copy or add a new method to the series. When a revised or new method is received, it is to be inserted in alphabetical order in the specified Part. It will be accompanied by a revised contents page. Both will carry the date of issue.

62314-0—1½

Furthermore, experience has shown that the art of assaying leads and inspires one to master many another honourable and profitable pursuit.

The longer one follows the art the further one is tempted to extend one's explorations.

Lazarus Erckers

INTRODUCTION TO
"A TREATISE ON ORES AND ASSAYING"
1572

Preface

Uranium milling now forms a major producing branch of the Canadian mineral processing industry, rivalling the outputs of the long-established copper, nickel and gold mills of the country, in the annual value of its product. This status has been reached in a very short time and the rapid growth of the industry has necessitated the training, as quickly as possible, of the staff necessary to man all the operations of the new plants.

Not the least important of these operations is the analytical control of the process. Few indeed are the analytical chemists with a background in the chemistry of uranium, and as a result it has been necessary for analytical chemists, untrained, or trained in other fields, to master in a very short time the separations and techniques required by the new materials and processes. Furthermore, some phases of uranium technology are still in a state of flux. New plants built will probably employ significantly different processes, these changes resulting from the improvements gained as a result of experience with existing plants, and from fundamental changes in process chemistry.

With the declassification of most of the previously secret details of refining process, there is a vast range of information available on all aspects of the subject. To one inexperienced in the field, however, this is almost as embarrassing as no information at all. There is at the present time, in fact, a dearth of practical works correlating the information on those subjects related to operating a uranium mill process control laboratory.

This Manual is an attempt to fill the need, and to provide, in addition to tested analytical methods, the auxiliary information which is so valuable in operating the laboratory efficiently. For example, the considerations involved in planning the laboratory to provide safe and efficient operation are of special importance in its proper functioning. In addition, a background of information on the chemistry of the ores and of the recovery processes can simplify the task of the analyst and aid in the intelligent discharge of his responsibilities. Finally, a knowledge of the sources of both sampling and analytical errors serves as a guide in providing reliable results and establishing the confidence which can be placed in them.

E. A. Brown,
Chief, Radioactivity Division.

Ottawa,
1958.

PART I

General Considerations

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Introduction

The production of uranium for use as a source of atomic energy began in 1942, and from the start Canada provided a considerable portion of this material. The uranium oxide supplied initially was produced at the Port Hope refinery of Eldorado Mining and Refining Ltd. from hand-cobbed ore and gravity concentrates. The ore and concentrates were of high grade and the nature of the process was such that adequate control was possible by classical analytical procedures.

By 1946 it had become evident that the production of high-grade ore and concentrates from the Eldorado mine at Port Radium, Great Bear Lake, would not be sufficient to meet the expected demand, and that expansion of the industry would involve utilization of relatively low-grade ores, including the material previously discarded at the Port Radium operation. Work was therefore started at the Bureau of Mines on the "Eldorado Project". This Project subsequently became the Radioactivity Division of the re-named Mines Branch.

In the beginning, this program was directed towards recovery of the uranium remaining in the gravity plant tailings of the Eldorado mine. Early work was hampered by the lack of a rapid, accurate method with sufficient sensitivity to determine the uranium content of the residues from leaching tests on low-grade ores, and to a lesser extent by lack of suitable methods for determining the many impurities and reagents whose concentrations were of interest in evaluating the various recovery processes. Accordingly, an important part of the program has been the investigation and improvement of analytical methods for the determination of a host of elements and ions in uranium-base materials. This work has been carried out in the Division's Analytical Section. The results of some of these investigations have appeared in various reports of the Division and in technical journals. Other investigations, however, previously published in connection with a different application, required no very great change in order to adapt them to this work, and mention of this fact has been confined to internal progress reports.

With the recent great expansion of the uranium milling industry, a definite need has arisen for a handbook or manual of analytical methods specifically selected for use in Canadian uranium plants. The present publication has been designed to fill this need.

The Division has investigated ores from all the major uranium mining districts in Canada (and indeed, from most of the deposits of possible economic interest), as well as the application of all the known methods of uranium recovery. The staff of the Analytical Section has therefore had considerable experience with the problems likely to be encountered in the control laboratory of most of the uranium process mills.

It was felt, however, that background information on such subjects as laboratory design, ore composition, sampling, and of course the chemistry of the processes themselves, would add to the usefulness of such a manual. An effort has been made therefore to cover these subjects in some detail, but the writer does not claim to be an expert in any of these fields, his primary purpose being to provide as complete a collection of analytical methods as possible.

No claim is made for the originality of any of the methods. They have been taken from a variety of sources and improved and adapted as required. There is no intention of implying that methods not included are not suitable or even that all the methods described will work on all the ores likely to be encountered. The methods have been used successfully in the laboratory, and in developing them, the greatest effort has been directed to reducing the length and complexity of those most frequently used. However, in the case of mills treating ores of one type only, it will be to the analysts' advantage to develop and adapt methods based on the known composition of the ore. Many of the methods can be shortened and simplified by eliminating separations for elements that are known to be absent. To this end, a description of the processes is given, as well as lists of the principal elements and minerals likely to be found in ores from the various regions. An attempt is also made to include references that provide more detail on the material covered here.

During the early part of the Division's history, the Analytical Section was under the able supervision of F. T. Rabbitts, who is responsible for the organization and direction that much of the work has taken.

The application of the fluorimetric method for uranium (which comprises the largest volume of work in the mill analytical laboratory) and of some of the other uranium methods, has been carried out by J. B. Zimmerman.

Most of the other methods have been developed or adapted by F. P. Roloson and R. J. Guest. Mr. Roloson has also written up many of the methods included in this manual. Other members of the staff, both past and present, have contributed to the methods and to our understanding of the chemistry that underlies them. In particular, J. A. F. Bouvier, A. D. King, A. Coote, D. Barkley, G. Hunt, E. Kornelsen, H. J. Herbst and A. R. Main should be mentioned. The drawings are the work of C. A. Josling of this Division.

It is a pleasure to acknowledge the kindness of Dr. C. A. Bennett of the General Electric Co., Richland, Washington, in permitting use of the example of a sample-blending problem from his book *Statistical Analysis in Chemistry and the Chemical Industry*. Thanks are also due to Dr. E. A. Bugbee of the Massachusetts Institute of Technology for permission to use the table which is taken from his book *A Textbook of Fire Assaying*. The cooperation of the publisher, John Wiley and Sons, Inc., of New York is also gratefully acknowledged.

The writer would also like to express his appreciation to Dr. E. A. Brown and H. W. Smith, Chief and Assistant Chief respectively, of the Radioactivity Division, who provided much assistance and encouragement.

Chapter 1

THE LABORATORY

FUNCTIONS

The following list summarizes the principal functions of an analytical control laboratory.

1. To ensure that the various operating variables (e.g. reagent concentrations and solution concentrations) are maintained at optimum levels.
2. To ensure that product purity is maintained.
3. To ensure maximum recovery of products.
4. To find the causes of difficulties when they occur.
5. To control the quality of reagents purchased and to permit the comparison of reagent prices on the basis of concentration of active ingredients.
6. To determine product grade, as a basis for payment.

Carrying out these duties involves most of the following operations: (1)

1. Organization and planning of the laboratory work (immediate, and long term).
2. Sampling.
3. Selection and testing of analytical methods.
4. Performance of analyses.
5. Measurement and control of precision and accuracy of analyses.
6. A knowledge of the interpretation and application of the results.
7. Provision of a general information service regarding composition of ores and products, and raw materials, and on process chemistry.

THE LABORATORY BUILDING

The first step in ensuring efficient operation is the designing and equipping of a suitable laboratory building. This includes not only the laying-out of benches and services, but the specification of suitable materials of construction for long trouble-free operation, and the location of the building on the site to minimize the distribution of chemical contamination and to reduce radiation background to acceptably low levels for radiometric determinations.

Some of the major considerations involved in planning a laboratory have been discussed by Coleman (2). The catalogues of suppliers of laboratory furniture can also be consulted, both as a guide to design and to suitable construction specifications for the bench and hood units. However, there appears to be little information available regarding the design of laboratories specifically for mining and metallurgical control analyses. As in most cases where a particular function is concerned, the laboratory must be laid out so that the various analytical determinations can be carried out as expeditiously as possible. The nature of the methods used, and the general distribution of the work, have been established for the various known processes and are not likely to change drastically for the life of present uranium contracts, so that flexibility is not a major consideration.

The largest volume of work is concerned with the determination of uranium in ores and residues. The most suitable method known at present for handling this determination is the fluorimetric method (Method U-1). Since this is basically a micro method, it is extremely sensitive to salting. It also involves some specialized apparatus and operations, all of which must be considered before arriving at a final floor plan. The sensitivity to salting, in particular, is of prime importance in locating the laboratory building and in deciding what operations to include in it. There is a tendency, particularly where level ground suitable for building is at a premium, to build the laboratory very close to, or as a part of the mill building. This also simplifies bringing the samples to the laboratory and the reporting of results. The contamination problem makes it most important that this be done with care so that traffic into the laboratory will not result in salting. In particular, in view of the friability of uranium minerals, which can result in higher grade dust from low-grade ore, the laboratory should not be located near open conveyor belts, the stacks of dust-collector systems (in case of damage to a bag filter) or even ventilator shafts of the mine itself.

For this reason too, it is considered undesirable to house sample crushing too close to the low-grade section of the laboratory. Crushing should be completely partitioned off from the laboratory itself by a dust-tight wall and entered by a separate outside door. A completely separate section must be provided for the preparation of concentrate samples, and this should be located preferably in the part of the mill where the final drumming of the concentrate occurs. Except for weighing out the sample, concentrate must never be handled in the laboratory, and if any special mixing is found necessary, completely enclosed equipment operating in an efficient fume hood must be used. A detailed description of sample preparation is given in Chapter 3.

In laying out the laboratory, the usual "motion study" considerations apply. The laboratory should be planned in such a way that each analyst can carry out his duties with a minimum of steps. Certain expensive or seldom-used equipment cannot be provided economically to everyone and such apparatus should be centrally placed with respect to those analysts using it most frequently.

Some operations present hazards, especially with regard to fire, such as charcoal-peroxide fusions, solvent extraction with flammable solvents, etc. and these must be so located as to minimize the danger to the laboratory and staff. Operations involving flammable solvents involve special considerations owing to the mobility of the vapours, and, if they comprise any significant portion of the laboratory's work, a separate room must be provided, with outside safety exit, vapour-proof electrical fittings and steam heating, as well as humidification and conductive flooring to minimize static electricity accumulation.

Fume Hoods

The necessity of evaporating solutions to complete dryness in the presence of sulphuric acid in many of the following analytical methods requires extremely efficient fume hoods with powerful exhaust fans. To remove such fumes successfully requires air face velocities of not less than 150 linear feet per minute. The efficiency of the fan drops over the useful life of the rotor as the result of corrosion and of accumulation of deposits on the blades, so that the installed capacity of the fan should be sufficient to provide over 200 linear feet per minute with a new rotor. A supply of spare rotors should be kept on hand and the rotor replaced when the fan becomes noisy, or when the face velocity of the hood drops below 150 linear feet per minute.

At least one special fume hood should be provided and kept exclusively for use with perchloric acid. It should be of non-porous construction and not

contain any wood, paint or other organic materials. It should be provided with a means for flushing with water both the rear of the baffles and the stack itself. It should preferably be exhausted by a Venturi-type blower, capable of providing the same face velocity as specified for the other hoods. Perchloric acid is so extremely useful in all types of ore analysis that it is impossible to consider doing this work without using it. It is equally impossible to consider employing the acid without at least taking the precaution of providing a suitably safe place to handle it.

Figure 1.1 gives a plan for a suitable laboratory building for a staff of 10 to 12. It must be emphasized however that it is purely hypothetical and is intended to illustrate some of the important considerations. It cannot be adapted to a particular application without consideration of the special factors involved.

Materials of Construction

A detailed discussion of this subject is beyond the scope of the present manual. It is important to give the matter serious consideration in planning so that too much time is not taken up later with repairs and incidental lost time. Thus regular kitchen-type construction is too light for benches; sinks and drains must be of genuinely acid-proof construction. Water lines should be copper. Floors should be covered with a resilient, resistant material and should be smooth (not corrugated) to permit thorough cleaning. Linoleum is satisfactory except in sections where much caustic is handled; in such sections, rubber or vinyl is preferable.

SAFETY

The general rules of safety for any analytical laboratory (3, 4) apply here as well, and should be strictly enforced. About the only special regulations required are:

1. The forbidding of pipetting by mouth.
2. The forbidding of the practice of eating lunches at the bench, and provision for thorough wash-up before eating.
3. The prevention of accumulation of large quantities of ore concentrates, or other material of high activity, in working areas.
4. Cleanliness in areas where materials of high uranium and thorium concentration are handled, to prevent ingestion of these elements.

Insofar as cleanliness is concerned, non-porous, easily cleaned bench tops should be used in areas where concentrates are handled. 'Arborite' or 'Formica' are recommended. As a further precaution, regular radiometric surveys with a suitable survey meter should be carried out to locate accidental spills.

The large dilutions required by some of the analytical methods will require instructing the staff in proper methods for mixing the contents of big volumetric flasks, since there seems always to be a temptation to swing these extremely thin-walled containers by the neck. Certain poisonous or otherwise dangerous reagents, while fairly frequently used in many laboratories, are used somewhat more commonly in uranium ore analysis and the laboratory staff should be made familiar with the precautions to be observed in handling them. Sodium peroxide (used in decomposing certain ores) is a vigorous oxidant and reacts violently with water. It must be kept in a dry place, away from combustibles, and particularly volatile solvents. In using it, safety glasses should be used and as much of the work as possible carried out with gloves and behind a safety shield.

Hydrofluoric acid, another reagent used in attacking refractory ores, can cause painful burns. Barrier creams should be applied to protect the skin,

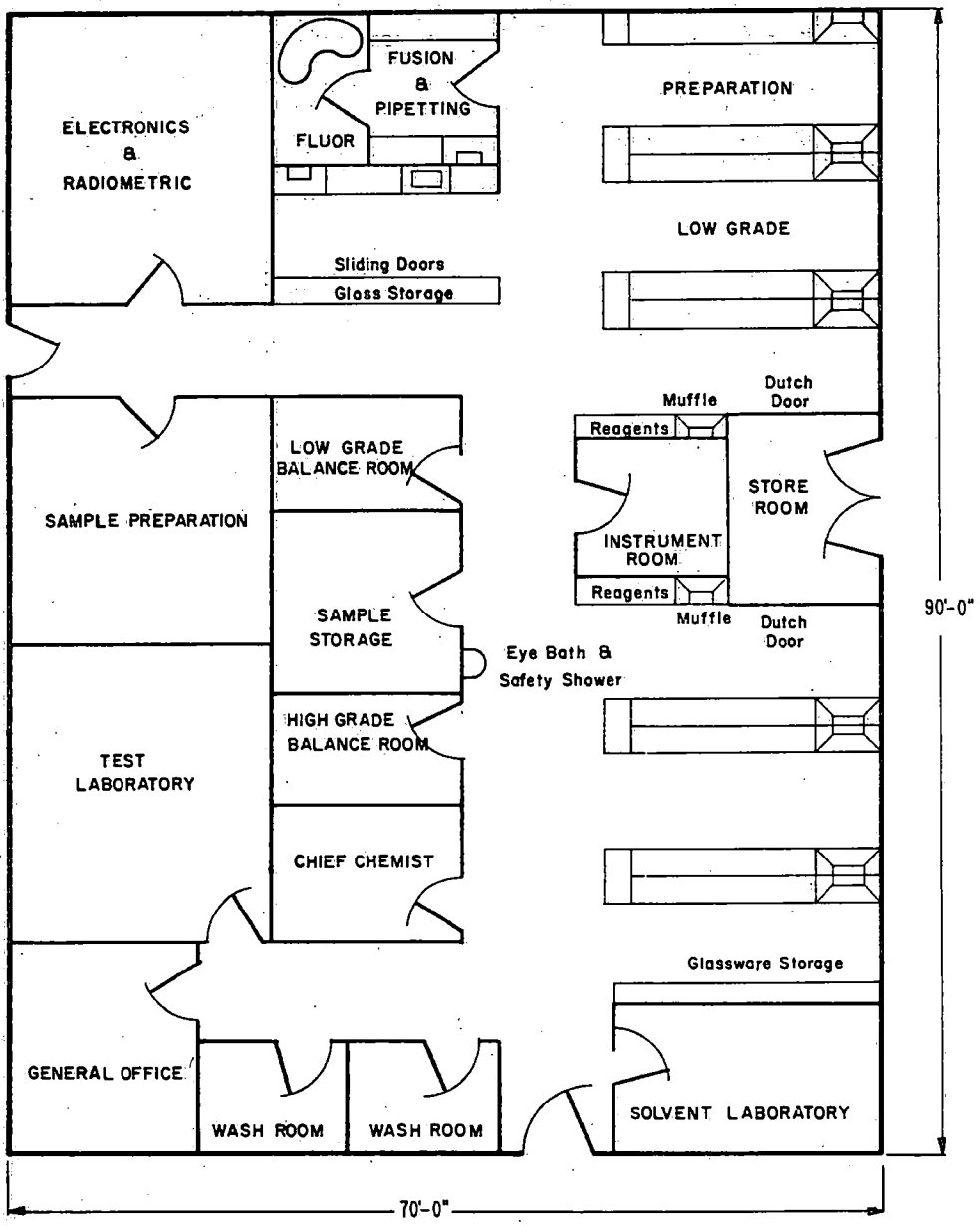

FIG. 1.1 – SUITABLE FLOOR PLAN FOR LABORATORY BUILDING.

particularly around the nails. The frequent use of borax and borax-type soaps is also recommended. Here again safety glasses should be worn.

The sodium fluoride used in the fluorimetric method is a systemic poison and precautions should be taken to avoid breathing or ingesting the powder. A hood for dispensing the pellets in fluorimetry, or the use of preformed tablets, is considered desirable.

Many of the various solvents and gases also have a deleterious effect and should only be used with adequate ventilation (i.e. in hoods with adequate face velocities). Examples are carbon disulphide, mesityl oxide, and chloroform (6).

Safety showers in accessible locations, eye fountains for washing the eyes in case of corrosive materials entering them, fire blankets and fire extinguishers should all be on hand. A first aid cabinet and a well-organized drill for handling accidentally injured people expeditiously are also important (7, 8).

The necessity for providing safe working areas for flammable solvents (2) and perchloric acid has been noted, but cannot be overemphasized.

USE AND CARE OF PLATINUM

The analysis of radioactive ores involves the liberal use of hydrofluoric acid, which necessitates stocking a considerable amount of platinum ware. This represents a large capital investment, and while platinum has a high scrap value (85% of the price of new platinum ware), most platinum articles are light-gauge and fragile. For this reason, platinum ware requires more care and attention than articles of glass or porcelain.

While platinum is not oxidized by air at any temperature nor attacked by any single acid, there are many chemicals that attack and damage it at comparatively low temperature.

The caustic alkalies, the alkaline earths, nitrates and cyanides, and especially the hydroxides of barium and lithium, attack platinum at a red heat. Molten sodium peroxide will dissolve platinum, but can be used in platinum vessels up to 480°C. without danger (provided that oxidizable substances are absent). Phosphorus and arsenic attack the hot metal so that phosphate and arsenate precipitates should not be ignited in their filter paper in the crucible. Silicon, which may be formed by the reducing action of carbon on silica, causes brittleness. Compounds of easily reducible metals, such as antimony, bismuth, copper, lead, tin, and zinc at high temperatures will result in the formation of low-fusing platinum alloys and all contact of platinum ware with these metals should be carefully avoided. Small pieces of solder are a particular hazard and for this reason no soldering should be permitted in areas where platinum is used. Heating platinum in the inner cone of a gas burner must be avoided, because of the possible formation of carbides, and because, since platinum is permeable to hydrogen and methane, some of the compounds mentioned above may be reduced to a form that attacks the platinum. Chlorine, chlorine oxides, some volatile chlorides and "aqua regia" attack platinum readily.

It is safe to use platinum for fusions with sodium carbonate, sodium carbonate plus sodium nitrate or nitrite, sodium borate, alkali fluorides and bifluorides, alkali bisulphate or pyrosulphate and alkali or alkaline earth chlorides in a neutral atmosphere (J. Lawrence Smith fusion). Solutions and mixtures of sulphuric acid, nitric acid and hydrofluoric acid may be boiled and evaporated, but *not* hydrochloric acid and nitric acid or hydrochloric acid with any other oxidizing agent.

Platinum should always be handled with platinum-tipped tongs. Platinum vessels should not be allowed to touch each other when hot since spot welding may occur. Hot platinum should always be placed on clean asbestos cement (transite) sheets to cool. Clean silica triangles should always be used to support the crucibles over the burner. (Nichrome or similar triangles should *not* be used.) The use of pyrophoric lighters for lighting gas burners should be avoided in the presence of platinum since they can deposit particles of incandescent metal.

Platinum ware should be buffed regularly with moist sea sand and burnished to remove the grey appearance that results from the loosening effect of the gas flame.

Fusing with borax, sodium carbonate, or potassium pyrosulphate followed by boiling in dilute hydrochloric acid removes many stains and impurities from platinum. Frequent use of the reshaper supplied by the manufacturer to restore the shape of platinum articles is recommended.

USE OF THE BALANCE

Weighing out Samples—Chainomatic balance (1-gram samples or more):— Place the weighing scoop on the left hand pan of the balance and the tare weight on the right hand pan. Lower the pan rests and lower the beam completely. Adjust the chain so that the pointer swings approximately an equal distance on each side of the zero mark of the index scale. Raise the beam, raise the pan rests and place the required weights on the right hand pan.

Raise the pan rests, and by means of a spatula, add the sample in small portions, lowering the beam slightly after each addition, until the pointer swings to the right instead of to the left. Raising the beam slightly each time, remove the sample from the scoop in somewhat smaller amounts until the pointer swings to the left, then add it to the scoop a few grains at a time by tapping the spatula. When the approximate balance point is reached, lower the beam completely and note in which direction the pointer tends to settle down. Repeat the above operation of raising the beam and adding or removing a few grains until the balance pointer swings approximately an equal distance on each side of the pointer. With practice a single weighing should not require more than 3 or 4 minutes. It is a waste of time to weigh the sample much more accurately than the remainder of the analysis justifies. Thus it is seldom necessary to weigh a gram sample to closer than 5 milligrams. However for the determination of major constituents, accurate weighing is necessary. If using a standard analytical balance (one having a sensitivity of 0.05 mg. per division swing is usually required), the method of swings should be used. At the Mines Branch, a constant-load, single-pan, semi-micro balance with optical indication of all weights less than 0.1 gram is used, which permits the weighing to be made very quickly and accurately. In this case an exact amount is not taken, but the approximate amount is transferred to a dry, tared, stoppered weighing bottle, which is then weighed on the balance. Details of the operation of this balance (the Gramatic) are given in the Fisher Scientific Co. Catalogue No. 111, pp. 34 & 35.

Good balances should be kept in a well-ventilated room separated from the laboratory and provided with doors. They should be kept clean and in adjustment. The balance should be on a solid table mounted on a vibration-free support. It should be away from heating radiators. It may be protected by a cover when not in use, but this should be *completely* removed when using (especially in the case of balances with externally cooled projection lamps).

Articles to be weighed should be at the temperature of the balance. Crucibles should be cooled 20-30 minutes in a desiccator, which need not have a strong desiccant in it. A vacuum-type desiccator is preferred since if a hot object has been placed in it, causing a partial vacuum in the desiccator, air can be allowed to enter gently without disturbing light precipitates.

If the precipitate is hygroscopic it should be weighed roughly, then re-ignited and weighed quickly.

CARE OF INSTRUMENTS

Most of the analyses described here require the use of complicated instruments, such as titrators, electrodeposition apparatus, fluorimeters and spectrophotometers. Apart from consideration of their initial expense and the cost of repairs, breakdown of these instruments can cause expensive delays in carrying out the analytical work. A good policy is to assign the care of the instrument to one individual in the laboratory, and provide him with a maintenance schedule and a special "maintenance record book" in which to record all service and repairs to the instrument. In this way, proper maintenance can be assured. In addition occasional checking of the record will bring to light any minor breakdowns which, when they occur too frequently, are symptomatic of major faults in the equipment.

CHECKING RESULTS

The bulk of the analytical work done in the routine analytical laboratory is carried on by technicians, often with only a rudimentary chemical background. A procedure must therefore be set up to ensure that all work can be checked. Figure 1.2 shows a form, set up on a rubber stamp, that can be used to enable analysts to record results in notebooks in such a way as to permit rapid checking of calculations.

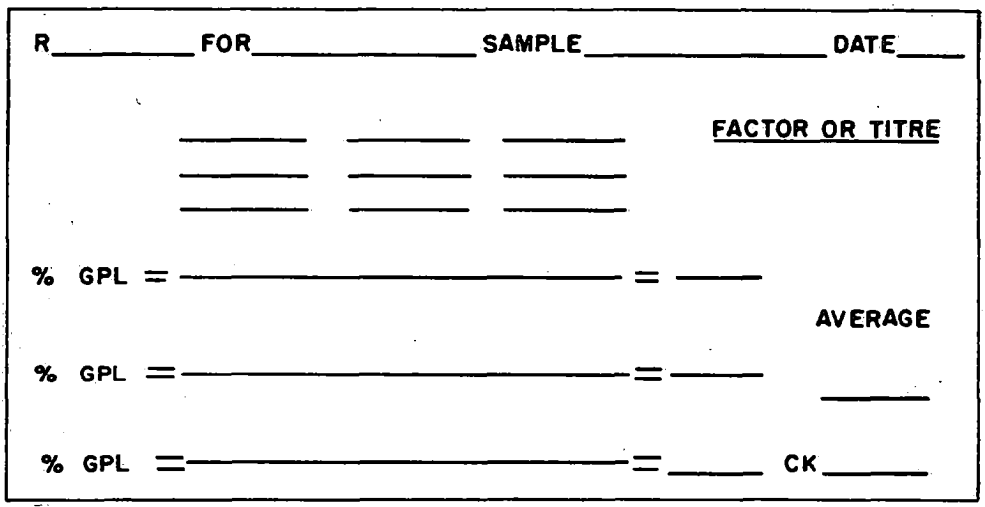

FIG. 1.2 - FORM FOR RECORDING RESULTS IN NOTE BOOKS.

To reduce errors in carrying out the analyses themselves, it is highly desirable that all methods be reduced to writing including every operating detail. In this way, the effect of the operator's technique, as a variable, can be largely eliminated.

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Chapter 2

URANIUM RECOVERY PROCESSES

GENERAL OUTLINE

The analytical methods included here are designed to cover, as far as possible, all types of samples likely to be encountered in any Canadian mill. It has been pointed out previously in the manual that some of them can be considerably shortened if it is known that particular groups of interfering elements are absent. The information contained in this chapter is intended to provide the analyst with the necessary background to decide how this can best be done.

In the following discussion, the processes are described and the analyses required are noted, together with the use to which the analytical result is put.

The principal processes are:

1. The Acid Leach Process, using
   a) Selective precipitation,
      i) by pH adjustment,
      ii) by use of selective precipitants.
   b) Ion exchange upgrading followed by precipitation.
   c) Solvent extraction followed by precipitation.
2. The Carbonate Leach Process, followed by direct precipitation.
3. Gravity and flotation concentration processes.

THE ACID LEACH PROCESS

Acid Leaching

It is, of course, possible to leach uranium ores with many acids. The process discussed here is that based on the use of sulphuric acid, since this is one of the few acids that it is economically feasible to use with low-grade ores. The process, which was developed originally for the treatment of gravity mill tailings from the Port Radium property of Eldorado Mining and Refining Ltd. (1, 2), uses sulphuric acid in concentrations sufficient to maintain acidities at a pH value below 2.0. Ores from the Bancroft area of Ontario, which contain uraninite and uranothorite as the principal uranium-bearing minerals, are readily leached by the same process using pH values in the range 1.5 to 2.0, as are ores in the Beaverlodge area of Saskatchewan. In the Blind River ores, the more refractory mineral brannerite (a complex uranium-titanate) usually predominates, and higher acidity is required. The pH values are low, about 0.5 or lower, and free acid concentration is a more suitable control than pH value, although the actual acid consumption is not high. If soluble arsenates and phosphates are present, the pH during leaching must be maintained below pH 2, since above this value, uranyl phosphates and arsenates precipitate. The presence of reprecipitated uranium in the residues may be determined by the method for determination of "secondary" uranium (Method U-2).

In general, ores are leached at the highest pH value possible (bearing in mind the conditions noted above), in order to minimize acid consumption. The

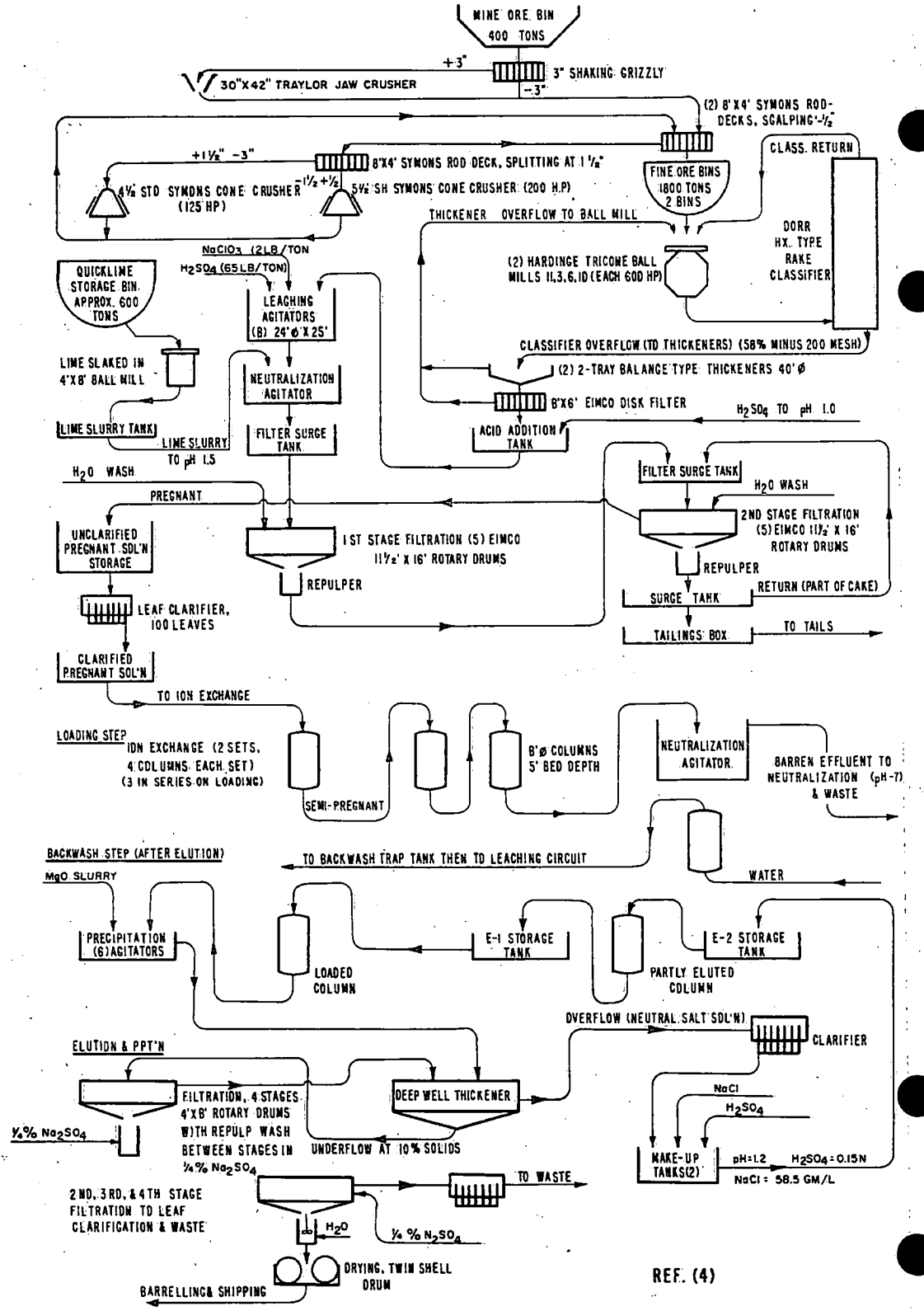

FIG. 2-1—FLOW SHEET OF A URANIUM MILL USING ACID LEACHING AND ION EXCHANGE.

acidity is maintained by recording pH controllers which automatically add 93% sulphuric acid as required, in the case of mills which use leaching conditions in the pH range 1.0 to 2.0. The operation of the equipment is usually checked at frequent intervals on dip samples by the operating staff, using regular line-operated pH meters. The electrometric method of pH measurement below pH 1.0 is less reliable. This is due to the fact that (pH being measured in logarithmic units) the actual acid concentration represented per unit becomes very large at low pH. In addition, suitable buffer systems for checking the instrument are not available. As a result, these processes are controlled by means of "Free Acid Determination" (Method F.A.-1), which is carried out on dip samples by operating personnel, and checked periodically by the laboratory.

Uranyl oxide (UO_3) dissolves completely in dilute sulphuric acid. Most unaltered uranium minerals, however, contain substantial amounts of tetravalent uranium. (Pitchblende, or its crystalline counterpart, uraninite, may contain 1/3 or more of the uranium as UO_2.) Tetravalent uranium will not dissolve at a useful rate at the higher pH values used unless an oxidizing agent is present to convert it to the uranyl form. An oxidizing agent is also necessary to overcome the effect of metallic iron introduced in grinding the ore. The iron is capable of reducing the uranium to the uranous state, in which it will precipitate as uranous phosphate or arsenate (if arsenate and phosphate are present in the pregnant leach liquor), even at pH values below 2.0. In this case it may be necessary to operate with a small excess of oxidant. If the amount of metallic iron is excessive, it may be necessary to analyze for it. No method is given in this manual, but the method of Riott (5) has been used for this purpose at some mines.

Many oxidants can be used in the process, but economic considerations make sodium chlorate the first choice for most operations in this country. It appears, incidentally, that in practice, the chlorate oxidizes the iron (which is always present in the leach liquor) to the ferric state, and it is this ferric iron which oxidizes the uranium, the chlorate serving to maintain the oxidation of the iron.

Ferric iron serves another purpose in the leach liquor, complexing arsenate and phosphate, thus minimizing the reprecipitation due to these ions. Ferrous iron does not act in this manner. Ferric iron so complexed, however, is not effective in the oxidation of uranous uranium and for that reason it may be necessary in some cases, as at Port Radium, to control the ferric iron content of the leach liquor to provide an excess of about 4 gm/l iron over that required to complex all the arsenate and phosphate present, in order to obtain maximum uranium extraction. It will thus be seen that arsenate and phosphate represent indirect consumers of chlorate.

Chlorate addition is controlled by regular determinations of total iron, ferrous iron (reducing power) and excess sodium chlorate (oxidizing power) by mill personnel, using the rapid control method (Method Fe-2). The iron determinations are checked by the laboratory, using the colorimetric methods (Fe-1 or Fe-4) or the volumetric method (Fe-3).

In solutions substantially free of phosphate or arsenate, the solution potential, as measured by a platinum electrode-saturated calomel half-cell combination is determined largely by the ferrous-ferric iron ratio (provided that sufficient amounts of the two ions are present). The E. M. F. of this system can therefore serve to indicate the ferric iron concentration, if pH and total iron concentration are constant. In practice this method of control has not been too successful, principally because of variations in these quantities and also in the sulphate concentration (since sulphate ion complexes ferric iron to some extent, reducing

its effective concentration). However it has been found that a potential (Pt : SCE) of about 400 millivolts indicates that satisfactory leaching conditions exist (6).

Composition of the Mill Feed

Orebodies are not homogeneous. The ore-bearing zone runs through barren country rock, and contains material which is too low grade to treat economically. In addition, it can contain material above the minimum grade as far as uranium content is concerned, but which must not be included in the mill feed for other reasons. The presence of large amounts of acid-consuming minerals is one reason for by-passing ore from a particular position of an orebody. Such carbonate minerals as calcite, magnesite, siderite and rhodochrosite consume acid. Their presence in the ore is determined from the carbonate content of the ore, using either the "acid evolution" method, C-1, or the "combustion" method, C-2.

From the reaction

$$Ca\ CO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

it is calculated that 1% CO_2 in an ore indicates an acid consumption of 44.5 lb. H_2SO_4 (100%) per 2,000 lb. of ore.

In addition to carbonates, certain aluminum and ferromagnesian silicates such as chlorite, and some metal oxides—e.g. the earthy form of hematite—are acid consumers. Specular hematite (common in ores from the Beaverlodge area) is not. If acid consumers of this type are suspected, the "neutralizing power" determination, N.P.-1, can be used to verify their presence.

Many sulphide minerals occur commonly in uranium ores, but most of these are not soluble in cold dilute sulphuric acid solutions. There is a considerable amount of pyrite (up to 2%) in the Blind River ores, and some of this consumes acid because of the higher temperatures and more concentrated acid used. Only a small percentage is dissolved, however. Pyrrhotite, marcasite, bornite and chalcopyrite are the principal sulphide minerals that consume acid.

From the reaction

$$FeS + H_2SO_4 \longrightarrow FeSO_4 + H_2S$$

it can be estimated that each 1% sulphur as pyrrhotite will consume close to 61 lb. sulphuric acid (100%) per 2,000 lb. of ore. The sulphur content of the ore may be determined by the gravimetric method, S-1, or the combustion method, S-2.

Apatite and fluorite are attacked to some extent, and the former consumes acid in the sense that the primary phosphates tie up hydrogen ion so that it is not available for leaching. It also complexes ferric iron required for oxidation of the uranous ion. Arsenates, which behave similarly, have been found in significant concentrations only in leach liquor from Port Radium ore.

For all acid-consumers including carbonate, the safest method for estimating acid consumption is bench-scale leach tests (3).

Some idea of the elements likely to be present in Canadian ores will be found in Tables 2.1 and 2.2. Properties of many uranium minerals are given in Table 2.3. Other related information is found in some of the references (7-14).

It is also necessary to analyze the ore from time to time for those elements whose presence in the leach liquor would interfere with the particular process being used for concentration of the uranium, or whose presence in the final precipitate might make it unacceptable to the purchasing agency. Examples of

Table 2.1

Concentration Range for Some Elements of Interest in Ores from the Major Uranium-Producing Fields*

Field	U_3O_8	Sec.† U_3O_8	ThO_2	As	P_2O_5	Fe	CO_2‡
Bancroft....	.08–.25	.01–.02	.05–0.3	0	.01–.36	1.2–9.0	<.01–.5
Beaverlodge.	.1 –.8	.05–.3	.002–.04	0–.04	.1–1.0	4–16	.2–4.5
Blind River..	.07–.23	.02–.03	.02–.07	.005–.02	.03–.08	3.3–10.1	.01–.4

Field	S	V_2O_5	Mo	TiO_2	Cu	Nb_2O_5	Ta_2O_5	Zr	F
Bancroft.....	.2–1.5		.005–.10			.07		.25	<.05–5.0
Beaverlodge..	.05–3.6	.01–.1	.003–.008	.04–.8	.02–.1	<.01			.04
Blind River..	2.5–10.2	.00–.03	.00–.02	.03–.05	.00–.7	<.02	<.02	.01	

* Gold and silver tested for in all cases, but only traces found.
† U_3O_8 soluble in hot Na_2CO_3 solution (Method U-2).
‡ Acid evolution (Method C-1).

the former are molybdenum, titanium and phosphate, which cause difficulties with the ion exchange process. Thorium and fluoride are examples of materials which are likely to carry through into the product.

A determination of the amount of acid-insoluble material in the ore is occasionally requested, as well as the total solids content of the liquor. Procedures for both are given.

The uranium content of the leached residue (leach tails) must, of course, be determined regularly as a guide to extraction being obtained. The "soluble loss", that is, the uranium lost in the filter cake due to incomplete washing, is found by determining the uranium content of the "rewashed final residue", a sample usually prepared by a member of the operating staff by repulping and thoroughly washing a portion of the "leach tails" with very dilute acid solution. One or other of these samples may also be analyzed for "secondary uranium", if it is suspected that some of the uranium may be reprecipitated after its initial solution, owing, for example, to excess phosphate or arsenate being present, or as a result of an unnoticed increase in pH.

The concentrated acid used in leaching must be checked occasionally. This is supplied or made as 93% H_2SO_4, since this concentration can be stored and moved in winter. Some mills produce their own acid from sulphur dioxide produced by burning either sulphur or pyrites. This may call for some analytical control. A procedure (S-1) gives methods for determining the sulphur content of crude sulphur and pyrites. The other analyses likely to be encountered, e.g. impurities in the sulphur or the Reich method for controlling the sulphur dioxide content of the burner gas, will be found in *Scott's Standard Methods of Analysis* (15). The reactions in acid leaching may be summarized as follows:

$$UO_3 + H_2SO_4 \longrightarrow UO_2SO_4 + H_2O$$

$$3UO_2 + 3H_2SO_4 + NaClO_3 \longrightarrow 3UO_2SO_4 + NaCl + 3H_2O \text{ (overall)}$$

or

$$3Fe_2(SO_4)_3 + 3UO_2 \longrightarrow 3UO_2SO_4 + 6FeSO_4$$

$$NaClO_3 + 6\,FeSO_4 \longrightarrow 3\,Fe_2(SO_4)_3 + Na\,Cl + 3H_2O$$

Table 2.2

Genetic Classification of Canadian Uranium Deposits*(7)

Group Type	Examples	Characteristic Elements	Characteristic Minerals	
			Uraniferous	Other
GRANITES, SYENITES (dykes, stocks, batholiths)	Bicroft, Dyno, Faraday, Rare Earths and Greyhawk mines	Th U Zr Si (Ce Fe P)	Uraninite, uranothorite, thorite, zircon, monazite, allanite, minor betafite	Magnetite, sphene
PEGMATITES	Viking Lake, Foster Lake, Richardson mine	U Th Nb Ta (Zr Si Ce P Fe F Ti Mo C)	Uraninite, allanite, pyrochlore, betafite, euxenite, samarskite, thucholite, etc.	Molybdenite, biotite, magnetite
METASOMATIC DEPOSITS a. General	Charlebois L., Beaverlodge Migmatites, Cardiff mine, Normingo	U Th Ce P Si (F Mo Fe S)	Uraninite, thorianite, thorite, monazite, rare earth silicates	Biotite, apatite, pyrite, fluorite, molybdenite, magnetite
b. Fenites	Oka deposits, Beaucage Mines basin property	U Th Nb (Ta Ce P F Ti Fe S)	Pyrochlore, betafite, perovskite	Calcite, soda pyroxene and amphibole, apatite, biotite, magnetite
HYDROTHERMAL DEPOSITS	Rocher de Boule, B.C., Gt. Bear Lake, Marian R., Beaverlodge camp, Theano Pt.	U C Fe (Cu Pb S V Se Co Ni As)	Pitchblende, thucholite	Hematite, quartz, calcite, chlorite, chalcopyrite, galena, pyrite, arsenides, selenides, nolanite
PLACERS	Cordillera of B.C. and Yukon	Th U Ce P Zr Fe (Nb Ta Ti W Sn)	Monazite, uraninite, pyrochlore, zircon	Magnetite, garnet, ilmenite, pyrite, etc.
CONGLOMERATES	Blind River, Ont.	U Th Ti Ce P (Cr Zr C)	Brannerite, uraninite, monazite, pitchblende?, thucholite	Pyrite, anatase, zircon, chromite traces of common sulphides, hydrocarbon, etc.

Sandstones	Middle Lake, Sask.	U Ca P	Autunite, phosphuranylite	Hematite
Phosphate Deposits	Fernie Group, Rocky Mountains	U Ca P C	Unknown	Collophanite, bitumen
Carbonaceous Deposits	Marine shales, lignite in Saskatchewan	U C H	Unknown	Bitumen, lignite
Gossan Cappings	On all hypogene deposits	Fe U Si Se V As S Al (Pb Cu Co Ni)	Uranophane, liebigite, zippeite, "gummite", etc.	Limonite, erythrite, malachite, etc.
Deposits Traversed by Meteoric Waters	Gunnar Mine (in part) Fish Hook Bay deposits	U Si S	Uranophane, secondary? pitchblende, thucholite?	Barite, gypsum

* Thorium $_{230}$ is always present as traces in uranium deposits because it is a product of radioactive decay of uranium. Thorium listed in this table includes thorium $_{232}$ only.

All radioactive deposits contain radiogenic lead. Lead is listed in this table only where significant amounts of "ore lead" are characteristic.

Table 2.3

The More Common Uranium Minerals*

Mineral	Chief elements present	U_3O_8 %	ThO_2 %	Usual colour	Usual lustre	Hardness and S.G.	Habit
Vein Minerals							
Pitchblende	Uranium Lead	To 91 usually to 80 in Canada	†	Steely black Black Greenish black Greyish black	Pitchy Dull	5–6 and 6–8	Massive Rounded Botryoidal Banded
Thucholite	Carbon Hydrogen Oxygen	Variable	†	Jet black	Brilliant Dull	3.5–4 1.77	Massive Nodules
Gummite	Uranium Lead	To 76	†	Yellow Orange Black	Dull Greasy	2.5–5 3.9–6.4	Massive Rounded Crusts Films
Uranophane	Uranium Silicon Calcium Lead	To 60	†	Yellow	Greasy Pearly	2–3 3.8–3.9	Massive Fine fibrous Crusts Films
Torbernite Metatorbernite	Uranium Copper Phosphorus	To 60	†	Green	Greasy Pearly	2–2.5 3.2–3.6	Small square tablets Micaceous Scaly
Autunite Meta autunite	Uranium Calcium Phosphorus	To 60	†	Yellow	Pearly	2–2.5 3.0–3.2	Like torbernite
Pegmatite Minerals							
Uraninite	Uranium Thorium Rare earths Lead	To 95 usually 80 in Canada	To 15	Black	Steely Dull Pitchy	5–6 8–10.6	Crystals Cubes Octahedra
Thorianite (uranoan)	Thorium Uranium Rare earths Lead	To 37 usually less	To 93	Black Greyish or brownish black	Sub-metallic	5–7 6.7–9.7	Crystals Cubes
Brannerite ‡	Uranium Thorium Rare earths Titanium Silica	To 43	0.3–4	Black to brown		4.8–5.4 4–5	Prismatic grains, usually metamict, and usually altered
Euxenite Polycrase Eschynite Priorite	Columbium Tantalum Titanium Rare earths Uranium Thorium	To 15 usually less than 10	To 17	Black Brown	Glassy Resinous	5.5–6.5 4.5–5.7	Massive Rough Crystal forms

* Ref. 13

† Negligible

‡ These data have been interpolated into the original table. The validity of brannerite as a mineral species has recently been questioned. Work in this Division appears to confirm its authenticity.

Table 2.3—Concluded

The More Common Uraniam Minerals—*Concluded*

Mineral	Chief elements present	U_3O_8 %	ThO_2 %	Usual colour	Usual lustre	Hardness and S.G.	Habit
Pegmatite Minerals—con.							
Pyrochlore Microlite Ellsworthite Hatchettolite	Columbium Tantalum Titanium Uranium Calcium	To 20	To 5	Black Brown Yellow	Vitreous Resinous	5–5.5 4.2–6.4	Rounded octahedral crystals or nodules
Fergusonite Formanite	Columbium Tantalum Rare earths	To 9	To 5	Black Brown	Vitreous Resinous	5–6 4–6	Tetragonal crystals Masses
Samarskite	Columbium Tantalum Rare earths Uranium Iron	To 20 usually 8–15	To 3.6	Black Brown	Vitreous Resinous	5–6 4–6	Rough crystals Massive
Uranothorite	Thorium Uranium Silicon Rare earths	To 27	To 50	Black Brown	Vitreous Dull	4–5 4–5	Tetragonal crystals Grains
Zircon Cyrtolite	Zirconium Silicon Rare earths	To 1.5	To 1	Brown Reddish Greyish	Vitreous Dull	3–7.5 3.6–4.7	Tetragonal crystals
Thucholite	Carbon Hydrogen Oxygen	Variable	Variable	Black	Brilliant Dull	3.5–4 1.77	Nodules Rough
Gummite	Uranium Thorium Lead	To 76	To 25	Orange Yellow	Dull Waxy	2.5–5 3.9–6.4	Massive Rounded
Uranophane	Uranium Silicon Calcium Thorium	To 60	To 3	Yellow	Greasy Pearly	2–3 3.8–3.9	Massive Fine fibrous

Table 2.4

Typical Analysis Required for Acid Leach Process

Sample	Analysis Required	Range % or gm/l	Frequency	Method
Feed	Uranium	0.05–0.5	daily composite monthly composite	U-1
	"Secondary" Uranium	0.005–0.2	occasionally	U-2
	Iron	1–10	daily composite	Fe-1
	Metallic Iron		occasionally	
	Arsenic		occasionally	As-P_2O_5-2

Table 2.4—Concluded

Typical Analysis Required for Acid Leach Process—*Concluded*

Sample	Analysis Required	Range % or gm/l	Frequency	Method
Feed—con.	Phosphorus		occasionally	As-P_2O_5-2
	Total Sulphur		daily composite (depends on area)	S-1 or S-2
	Sulphate Sulphur		daily composite (depends on area)	S-1
	Sulphide Sulphur			by difference
	Carbonate		daily composite	C-1 or C-2
	Graphite		occasionally	by difference
	Acid Insoluble			A.I.-1
	Screen Analysis			
Feed sample screen fractions	Uranium	0.001–1.0	occasionally	U-1
Leach liquor	Uranium	0.5–5	daily composite	U-1 or U-3
	Total Iron	1–10	daily composite	Fe-2
	Ferric Iron		daily composite	Fe-1
	Ferrous Iron		daily composite	by difference
	Oxidizing Power		daily	Fe-2
	or Reducing Power		daily	Fe-2
	In some areas:			
	Free Acid		daily	F.A.-1
	Arsenic		daily	As-P_2O_5-2
	Phosphorus		daily	As-P_2O_5-2
	Thorium		daily	Th-2
	Titanium		occasionally	Ti-1
	Molybdenum		occasionally	Mo-1
	Fluoride		daily	F-1
Residue	Uranium	0.001-0.05	daily composite monthly composite	U-1
	Secondary Uranium	0.001–0.05	occasionally	U-2
	Arsenic		occasionally	As-P_2O_5–2
	Phosphorus		occasionally	As-P_2O_5–2
	Thorium		occasionally	Th-1
	Titanium		occasionally	Ti-1
	Fluoride		occasionally	F-1
	Acid Insoluble		occasionally	A.I.-1
Residue screen fractions (In conjunction with feed screen fractions)	Uranium	0.001–0.1	occasionally	U-1
Rewashed final residue	Uranium	0.001–0.05	daily composite	U-1

Recovery of Uranium:

Direct Precipitation

The simplest method for uranium recovery is to precipitate uranium hydroxide, hydrous uranium oxide, or a diuranate by raising the pH of the leach liquor beyond the precipitation point for uranium. A cheap neutralizing agent such as caustic, ammonia, or magnesium hydroxide is used. Lime is not suitable since the calcium sulphate formed dilutes the product and lowers the grade. Many cations present in the liquor will precipitate, but some of these (e.g. ferric iron) can be precipitated first by raising the pH to an intermediate value, holding it there until the impurities have precipitated, then filtering. The uranium can then be precipitated in the filtrate. Precipitation pH data can be obtained in Britton's book (17). In general, this method has not proved practical.

A modification, in which ferric iron is first reduced to ferrous iron has shown some promise. Ferrous iron precipitates at a fairly high pH and in this way uranium can be precipitated in a single stage. The process is expensive and is only justified if a reasonable concentration (e.g. 5 gm/l) of uranium is present in the liquor.

Complexing impurities by means of organic chelating agents followed by precipitation of uranium by pH adjustment is also technically possible, but has not so far proven economical.

Precipitation After Prior Reduction of Uranium

Hexavalent uranium does not form many insoluble compounds. By reduction to the uranous form, which resembles thorium in its chemical properties, a number of precipitation methods become available. Reduction can be carried out using reagents such as sodium hydrosulphite, metallic aluminum or zinc. Iron, however, is not too effective. The reduced uranium can then be precipitated as the phosphate, arsenate, or fluoride, among others.

The Aluminum Reduction Process (1)

On addition of powdered aluminum metal to an acid leach liquor at about pH 2.0, uranyl ion is reduced to the uranous state. If phosphate or arsenate ions are present in the solution, the uranous ion then precipitates to give a precipitate containing 30-45% uranium as U_3O_8. Some ions such as copper and bismuth precipitate as the metal. Thorium, if present would also precipitate when the phosphate is added. If phosphate is already present in the liquor the thorium would remain with the residue.

The optimum conditions for the precipitation are a temperature of 20°C. and a pH value of 1.5 to 0.75. The $(As + P_2O_5) / (U_3O_8)$ ratio should be in the range 0.5 to 1.0. The arsenic + phosphorus content is determined by Method $As–P_2O_5 – 2$ and the uranium content by the colorimetric thiocyanate or sodium hydroxide-peroxide method using ethyl acetate extraction (Method U-3).

The amount of aluminum to be added is based on the oxidizing power of the solution (Method Fe-2). From the titration calculated as ferric iron or sodium chlorate, the equivalent amount of aluminum is determined, and an empirical excess of 0.3 – 0.5 gm/l is added to the value obtained. For Port Radium leach liquor (U_3O_8 1.5 – 2.0 gm/l, Fe^{+++} 3.0–5.0, $NaClO_3$ 0.0–0.3) the amount of aluminum required, including the excess, is 1.0 to 1.3 gm/l.

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Some of the reactions involved in this process are:

$$3\ Fe^{3+} + 2\ Al \longrightarrow 3\ Fe^{2+} + 2\ Al^{3+}$$
$$Cl^{5+} + 2\ Al \longrightarrow Cl^{-} + 2\ Al^{3+}$$
$$3\ U^{6+} + 2\ Al \longrightarrow 3\ U^{4+} + 2\ Al^{3+}$$
$$3\ Cu^{2+} + 2\ Al \longrightarrow 3\ Cu + 2\ Al^{3+}$$

Aluminum is also consumed in hydrogen evolution:

$$3H_2SO_4 + 2\ Al \longrightarrow Al_2(SO_4)_3 + 3\ H_2.$$

The final product is believed to be a mixture of two acid salts having one or two mols of arsenate or phosphate per mol of UO_2. The proportion, which depends on the final pH, is represented by the following equation:

$$UO_2\ P_2O_5\ 2H_2O \rightleftharpoons UO_2\ \frac{P_2O_5}{2}\ \frac{H_2O}{2} + H_3PO_4$$

The precipitate obtained is quite impure. It can be further upgraded by leaching out the arsenic, phosphate and copper by means of a treatment with hot caustic, leaving sodium diuranate in the precipitate.

Table 2.5

Typical Analysis Required for Aluminum Reduction Process

Sample	Analysis Required	Range % or gm/l	Frequency	Method
Leach liquor	See Table 2.2			
Barren solution	U_3O_8	0.01–2.0	several times during course of precipitation	U–3
	As + P_2O_5	1.0–1.5	once during course of precipitation	As–P_2O_5–2
Product	U_3O_8	30–40	once	U–4
	As	10	per	As–1
	P_2O_5	6	batch	P–1
	Cu	2–4	or	Cu–1
	Al	4	lot	Al–1
	S/SO_4	2		S–1
	Moisture	5–15		M–1

The Ion Exchange Process (18, 19, 23, 24)

The aluminum reduction method, while extremely convenient for use on liquors from an ore high in phosphate or arsenate, is less satisfactory for other ores. The expense of adding phosphate, which must subsequently be removed at the refinery, must be considered, and the precipitation barren solution often contains appreciable uranium values.

The use of an anion exchange resin to recover uranium from acid sulphate leach liquors has therefore been adopted by most Canadian concentrating plants. The ion exchange method provides almost complete recovery of uranium, at high grade, and relatively free from impurities. Depending to some extent on the location of the mill, the process is economically competitive with the other methods and in some areas has a definite economic advantage.

The process depends on the formation, in acid sulphate solution, of a uranyl sulphate anionic complex during the passage of the solution through a strong-base anion exchange column (such as Amberlite IRA-400, Dowex 1, Permutit SK, Deacidite FF, etc.). The uranyl sulphate complex so formed has been shown to be mainly $UO_2(SO_4)_3^{4-}$ and the mechanism of the reaction is given by

$$UO_2^{2+} + 3\,SO_4^{2-} + 4\,RCl \rightleftharpoons R_4UO_2(SO_4)_3 + 4\,Cl^-$$

where R Cl is the chloride form of the resin and

$$UO_2^{2+} + SO_4^{2-} + 2\,R_2SO_4 \rightleftharpoons R_4UO_2(SO_4)_3$$

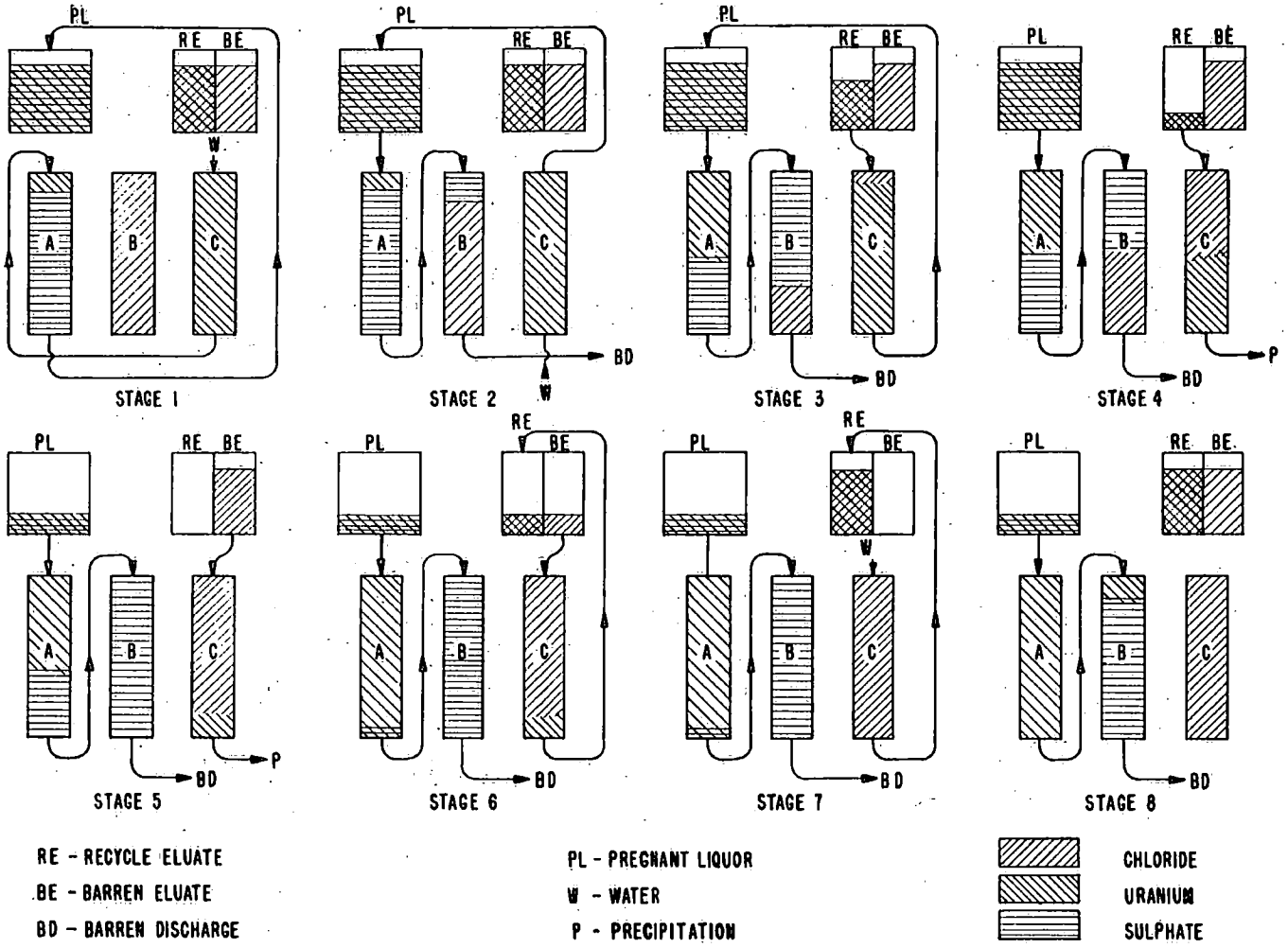
where R_2SO_4 is the sulphate form of the resin.

The resin bonds indicated are referred to as exchange sites. Possession of these sites is the distinguishing characteristic of an ion exchange resin. A definite quantity of a given resin will have a definite number of these sites. Anions are absorbed stoichiometrically by the resin, therefore, and it may be considered as having an equivalent weight. This equivalent weight is spoken of as the "capacity" of the resin and is usually stated in terms of milliequivalents per gram of dry resin. The capacity of commercial resins is 3.0 to 3.5 milliequivalents per gram of dry resin or 1.2 to 1.4 meq per ml, and, since the principal uranium complex is tetravalent, a theoretical capacity of 245 mg U_3O_8 per gram of dry resin (or 98 mg U_3O_8 per ml.) is possible. Higher loadings are obtainable from concentrated uranium solutions owing to a change in the proportion of the complexes absorbed.

Adsorption

The process may be briefly described as follows. The sulphuric acid solution resulting from the leaching of the ore, containing 0.5 to 3 grams U_3O_8 per litre, ferric iron, aluminum and magnesium along with other impurities derived from the ore, is adjusted (for example, with lime) when necessary to a pH in the range 1.2 to 2.0, preferably 1.5 to 1.8, and is clarified and passed through two or more ion exchange columns (of a set of three or more). The solution is passed continuously until the uranium content of the effluent ("barren") from the last column rises to a value 1% of that of the pregnant liquor fed to the first column. This point, called "breakthrough", is determined by one of the rapid methods listed. The flow rate of the leach liquor through the resin is so related to the rate of the uranium adsorption process, that ideally, the first or "lead" column will just be saturated with uranium at the breakthrough point. Samples (called "lead column" and "end column" samples) are now taken. The first column is taken off the leach liquor stream, which is now directed through the second or "end" column. This column becomes the new "lead" column, and the next column in the series, which has been eluted free of uranium and washed, is cut in as the new "end" column. This procedure is then repeated, the piping of the columns being so designed that when the last column in the series is reached, the first column can be connected as the "end" column.

In another method of operation, now gaining in acceptance, three columns of a 4-column set are used in series for the loading cycle. The first column is cut out and switched on to elution when it is saturated, as determined by comparing the uranium content of the ion exchange feed liquor and the effluent from the first column, using the thiocyanate colorimetric method (U-3), usually without the preliminary ethyl acetate extraction. The Bausch and Lomb Spectronic "20" spectrophotometer is often used for this determination. When this type of operation is used, it is no longer necessary to check for breakthrough on the last column. There is also less risk of loss of uranium if breakthrough is passed and hence timing is not so important.



Stage 1 Downwash C

Stage 2 Backwash C
Loading A + B

Stage 3 Highgrade Elution (Displacement) C
Loading A + B

Stage 4 Highgrade Elution C
Loading A + B

Stage 5 Recycle Elution (Displacement) C
Loading A + B

Stage 6 Recycle Elution (C)
Loading A + B

Stage 7 Downwash C
Loading A + B

Stage 8 Standby C
Loading A + B

FIG. 2·2 - FLOW DIAGRAM FOR THREE COLUMN ION EXCHANGE URANIUM EXTRACTION PLANT.

REF. (11)

The lead column, which is saturated with uranium (about 4 lb U_3O_8/cu. ft. resin) is now washed *upflow*, to remove fine ore particles and hydrolytic precipitates (the process is called "backwashing"). This backwash is measured and sampled, as a control on possible uranium losses.

Sampling and Analysis, Adsorption Part of Cycle

Samples of the composite pregnant leach liquor and the composite barren effluent are analyzed to determine the recovery of this part of the overall circuit. These pregnant liquor solutions can be analyzed colorimetrically by either the thiocyanate (if thorium is present) or by the peroxide method after an ethyl acetate-aluminum nitrate separation. The barren solution will be analyzed fluorimetrically. The ratio of quenchers to uranium is always high in this solution, and if cerium, manganese or iron are present in large amounts, an ethyl acetate separation will be required here also.

Total iron determinations (Method Fe-1) may be required on these solutions. Thorium, if present will have to be determined occasionally, (Method Th-2). Other ions, such as titanium (Method Ti-1), zirconium (Method Zr-1) niobium (Method Nb-1), and tantalum (Method Ta-1) which interfere by forming hydrolytic precipitates in the resin beads, may be present in the liquor. The acid leaching of certain sulphide ores may result in the formation of polythionates unless certain precautions are taken, and these anions are adsorbed by the resin irreversibly to create a serious poisoning problem. They are determined in the liquor by Method S_nO_6-1. Arsenic and phosphorus (Method As-P_2O_5-2), chlorate (Method Fe-2), chloride (Method Cl-1), fluoride (Method F-1) and copper (Method Cu-1) are other ions whose determination will be required in the treatment of certain ores.

Elution

The uranium on the saturated column is then removed ("eluted"). This is usually done in two steps, owing to the nature of the elution curve (Figure 2.3). The bulk of the uranium moves off in the first half of the elution, but to achieve 99% recovery, elution must be continued for an equal period. To reduce the volume of eluate sent to precipitation and increase the concentration, the eluting solution from the second half of the elution (called "recycle eluate") is used for the first half of the next elution. The eluate from the first half of the elution ("pregnant eluate") moves to precipitation. After precipitation, the filtrate is made up with the required reagents to replace those used in elution and precipitation and is then called "barren eluate". It is used for the second half of the elution. The eluting solution can be a solution of almost any mineral salt, acidified to prevent the precipitation of uranium in the resin bed. In practice the systems used consist of molar solutions of the sodium, magnesium, or ammonium salts of nitric and hydrochloric acids, acidified either with the respective acids or with sulphuric acid, at concentrations in the range 0.05 to 0.15 normal. Since the uranium goes on the resin as the anionic sulphate complex $UO_2(SO_4)_3^{4-}$, four equivalents of the eluant (viz. NO_3^- or Cl^-) are taken up by the resin, and three SO_4^{2-} groups appear in the eluate, for each UO_2^{2+} group eluted. The sulphate content of the eluting solution therefore builds up very rapidly unless it is removed by a two-stage precipitation scheme (*see* Precipitation). If not removed, the sulphate eventually levels off due to inherent or intentional bleeds in the elution-precipitation circuit, at values from 100-150 gms SO_4 per litre. Since the presence of sulphate in the eluant reduces the elution rate and prolongs the duration of the elution part of the cycle, it is determined regularly in the various solutions. The uranium content of the recycle eluate and the pregnant eluate (precipitation feed) is also determined. Since these solutions are relatively pure, with iron the only interfering ion, these analyses can be carried out directly

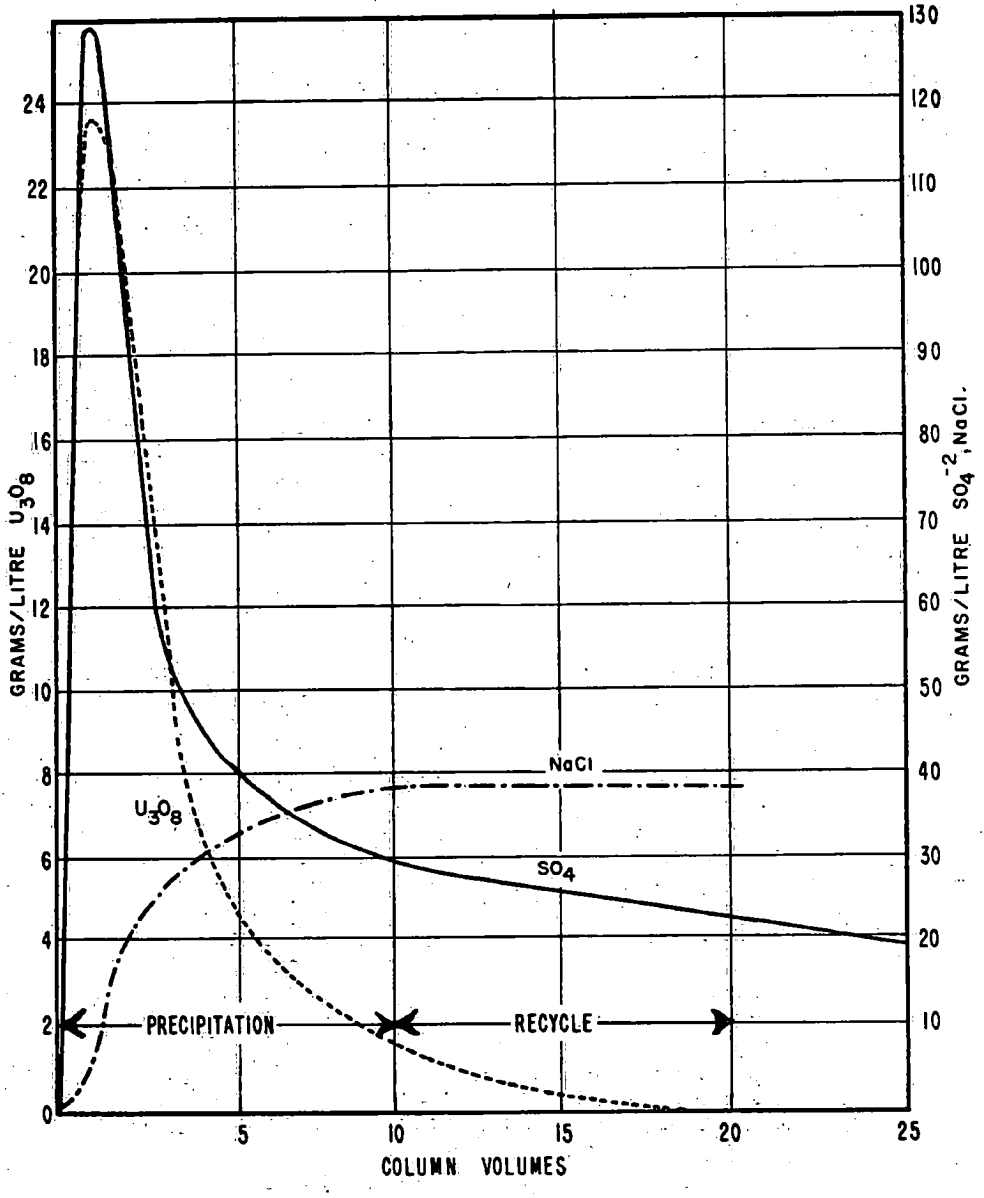


FIG. 2.3—TYPICAL ELUTION CURVES ($NaCl$-H_2SO_4) (SHOWING CONCENTRATION OF THE VARIOUS IONS IN THE ELUATE AS A FUNCTION OF THE VOLUME OF ELUATE PASSED) REF: (2)

by the thiocyanate procedure without prior separations. In some cases, uranium assays may also be required on the barren eluate, if precipitation or filtration is not efficient. These samples would ordinarily be analyzed fluorimetrically. The "elution nil spot", the point at which elution is virtually complete, is also followed to verify that the efficiency of the eluant remains unimpaired. This point is usually taken as the point at which the eluant uranium concentration drops below about 0.1 gm U_3O_8/l. A convenient method of doing this is to use the ferrocyanide spot test. However, this method appears to give erratic results in nitrate solutions and here use of the thiocyanate method would again be indicated.

Precipitation of the Product from the Eluate

Uranium is recovered from the pregnant eluate solution (from any of the acid eluting systems) by raising the pH to about 7. The same reagents and other considerations apply that are discussed at an earlier point in this chapter under "Direct Precipitation". In some plants, two-stage precipitation is employed, using lime to raise the pH to 3.0 – 3.5. This precipitates most of the iron, a good part of the thorium, and bleeds some of the sulphate. The first-stage precipitate, to which frequent reference will be found in this manual, is called the "iron cake" or more properly, "gypsum cake", and consists largely of calcium sulphate. It must be analyzed for uranium and thorium. This product will normally be returned to the leaching step, to recover any uranium which has precipitated at this point. Uranium is recovered from the filtrate by using magnesia, caustic or ammonia to raise the pH to 7.0.

If single-stage precipitation is used the pH is raised to 7.0 directly using magnesia, caustic or ammonia.

In all cases magnesia gives a more easily filterable precipitate in the cold. On the other hand, addition is harder to control, precipitation is slower, and the product is often of lower grade.

After precipitation, the concentration of the eluting ion (chloride or nitrate) is adjusted, the acidity is brought back to the desired value, and the solution returns to the process as "barren eluate".

Make-up of the barren eluate requires determination of its nitrate or chloride content, depending on the system being used. Methods NO_3–1 or Cl–1 are used at the Mines Branch for this purpose. When a mixed system is used, e.g. sodium chloride as the eluant and magnesium hydroxide as precipitant, determination of the magnesium and of the sodium may be required from time to time to follow the change in the ratio of these two ions with a view to correlating it with eluting efficiency.

The analyses required on the product are discussed at the end of the chapter.

Examination of the Resin

From time to time there may be evidence of deterioration in the performance of the ion exchange columns, which indicates the necessity for remedial action. There are a number of reasons why this may occur, some of which are related to the condition of the resin itself. For this reason, samples of the resin will need to be analyzed from time to time for the common poisoning ions. These include ash, silica, molybdenum, phosphate and polythionates. The methods are assembled under one heading, Method $A.X_2$-1.

Table 2.6a

Typical Analysis Required for Ion Exchange Process

Sample	Analysis Required	Range % or gm/l	Frequency	Method
Feed				
(Leach liquor)	U_3O_8	1–3	1/day	U-1 or U-4
Daily composite	Fe^{3+}	3–10	"	Fe-1
	Fe^{2+}	0–5	"	Fe-1
	ClO_3	0–0.3	"	Fe-2
	Cl	0–0.4	"	Cl-1
	SiO_2	0.3–1.0	occasionally	Si-1 or Si-2
	S_nO_6	0.0–0.05	depending	S_nO_6–1
	ThO_2	0.0–1.0	on ore	Th–2
	TiO_2	0.00–0.05	being leached	Ti-1
	V_2O_5	0.0–0.01	"	V-1
	F	0–0.5	"	F-1
	$As + P_2O_5$	0–0.5	"	$As-P_2O_5$-2
Cycle composite	U_3O_8	1–3	2 to 3/day	U-1 or U-4
Barren effluent				
Daily composite	U_3O_8	0.005–0.01	1/day	U-1
	Cl	0.5–1.0	"	Cl-1
Cycle composite	U_3O_8	0.005–0.01	2 to 3/day	U-1
Recycle eluate	U_3O_8	0.5–2.5	2 to 3/day	U-1
High-grade eluate	U_3O_8	5–10	2 to 3/day	U-4
Backwash	U_3O_8	0.1–0.5	1/day	U-1
Precipitation feed	U_3O_8	5–10	1/day or 1 per batch	U-4
(Composite eluate)	Fe(tot)		"	Fe-1
	S/SO_4	15–50	"	S-1
	ThO_2		"	Th-1
Gypsum or "Iron" cake	U_3O_8	0.1–2.0	1/day	U-1
	Fe	0.5–5	"	Fe-1
	Cl	0.5–1.5	"	Cl-1
	S/SO_4	15–20	"	S-1
	ThO_2	0–2	"	Th-1
	Neutralizing power	0.5–1 meq/dry gram		NP-1
	CaO	20–30	"	
Product	*See* Table 2.10			
Barren eluate	U_3O_8	0.005–0.05	1/day	U-1
	Cl or	20–30	"	Cl-1
	NO_3	40–60	"	NO_3–1
	S/SO_4	25–35 (1 stage ppt'n.) 2–10 (2 stage ppt'n.)	"	S-1
Used resin	Salt splitting capacity	2.5–3.5 meq/dry gram		
	Weak base capacity	0.1–0.5 meq/dry gram		
	Uranium capacity breakthrough	30–50 g/l wsr		
	Uranium capacity saturation	50–70 g/l wsr		
	Moisture	40–50	Once every 3 months or oftener depending on impurities in ore.	
	S_nO_6	0.1–10		
	Sulphated ash	0.5–10.0		

Table 2.6a—Concluded

Typical Analysis Required for Ion Exchange—*Concluded*

Sample	Analysis Required	Range % or gm/l	Frequency	Method
Used resin—con.	Silica	0.05–5.0		
	Other impurities			
	P_2O_5			
	Ti			
	Th			
	Zr		As required	

Table 2.6b

Typical Analysis Required on Reagents Used in Ion Exchange

Sample	Analysis Required	Range
Salt	Cl	> 99.7% NaCl
	Insol.	< 0.2%
	B	< 0.005%
Sodium sulphate	SO_4	> 97% Na_2SO_4
	Na_2CO_3	< 0.25
	Organic matter	< 0.01
	Insol.	< 0.2
Sodium nitrate	NO_3	99 + as $NaNO_3$
	Insol.	< 0.2

Table 2.6c

Typical Analysis Required on Some Common Reagents—Ion Exchange Precipitation

Sample	Analysis Required	Range
Magnesia	MgO	75–85
	CaO	5–10
	R_2O_3	1–5
	SiO_2	1–5
	Loss on ignition	1–10
	B	0.001–0.015
Lime	CaO	70
	MgO	1
	R_2O_3	0.5
	Acid insol.	1
	S	0.5
	B	0.001–0.01
Sulphuric acid	H_2SO_4	91-95
	HNO_3	< .005
	HCl	< .005
	NH_4	< .001
	Fe	.04
	Pb	.006
	Residue on ignition	.05
	Substances reducing $KMnO_4$ (SO_2)	< .001
	P_2O_5	< .01
	B	< .005

Glossary of Ion Exchange Terms as used at the Mines Branch, Ottawa

Backwash—The upward flow of water through a resin bed to clean and reclassify the bed after exhaustion.

Barren effluent—The solution almost completely denuded of uranium (> 99%) that emerges from an ion exchange column on adsorption.

Barren eluate—The filtrate after neutralization to pH 7.0, made up to a required salt and sulphuric acid concentration, ready for recycling on the second half of elution.

Bed volume—The volume of the wet settled resinous material plus voids in the column after the exchanger has been properly conditioned for effective operation. The use of this term permits comparison with columns of any size.

Bleed—The phenomenon in which some of the influent ions are not adsorbed and appear in the effluent when a solution is passed through an under-regenerated exchange resin bed.

Cycle—In a four-column system.

1. Exhaustion as end column
2. Exhaustion as lead column
3. Displacement wash
4. Backwash
5. Elution
6. Displacement wash

In a four-column system, there are four loading and elution cycles for each resin cycle.

Displacement wash—The introduction of an influent solution A to displace solution B in the voids of the resin bed as effluent.

Elution—The stripping of adsorbed ions from an ion exchange material by the use of solutions containing other ions in concentrations higher than those of the ion to be stripped.

Exhaustion point—The state at which the adsorbing resin is no longer capable of useful ion exchange.

l. wsr—Litre of wet settled resin.

Nil spot—A spot test with potassium ferrocyanide ($K_4Fe(CN)_6$) indicates approx. 0.1 gm U_3O_8/litre.

Retention time (R.T.)—The total time required for an increment volume of solution to pass through the column.

$$\text{R.T.} = \frac{\text{void volume}}{\text{flow rate}} \qquad \text{Void volume} = 40\% \text{ of resin volume}$$

Solvent Extraction Processes

Recently, the use of selective liquid extractants for the recovery of uranium from sulphuric acid leach liquors has been introduced. These fall into two classes, those using hydrocarbon solutions of alkyl amines and those using hydrocarbon solutions of alkyl phosphate esters and other phosphorus compounds.

Phosphate Ester Processes (25, 26, 27)

The phosphate esters, both in extraction and in stripping, behave somewhat like selective liquid cation exchange resins. They include mono-, di-, and tri-

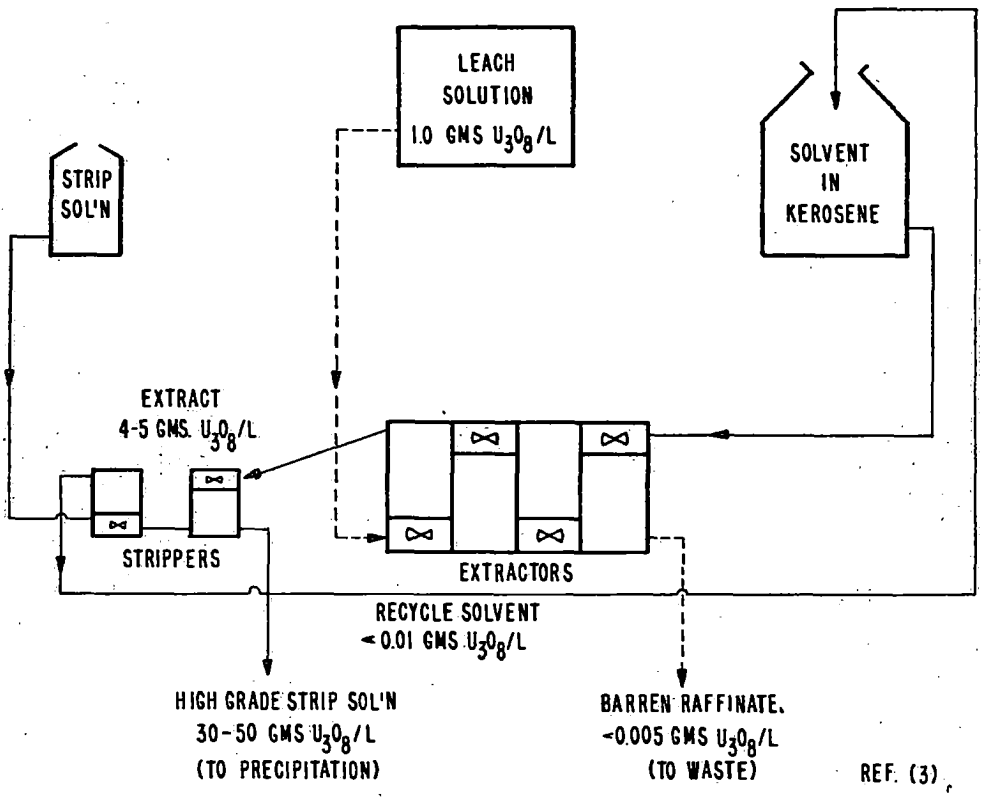


FIG. 2·4 - FLOW DIAGRAM OF SOLVENT EXTRACTION PILOT PLANT.

alkyl phosphates, alkyl phosphoric and phosphenic acids and their esters. Alkyl phosphites, phosphine oxides and alkyl diphosphates and diphosphonates have also been proposed. The most completely investigated of these is the process employing dodecyl phosphoric acid (a monalkyl phosphoric acid ester of 2-, 6-, 8-trimethyl nonanol) and that using di (2-ethyl hexyl) phosphoric acid.

The didodecyl phosphoric acid process, developed by the Dow Chemical Co., Pittsburg, Calif., and the U.S. Bureau of Mines at Salt Lake City (24), uses a 0.1 M solution of the reagent in kerosene which is prepared in the plant from the alcohol and phosphoric acid. This extractant is contacted with the leach liquor in apparatus like that shown in Figures 2.4 and 2.5. Good uranium extraction is obtained over a wide pH range. However, extraction of Ti and Th is high at pH 1 and below; hence pH 1.5 is optimum.

The ferric iron content must be kept below 1 gm/l, otherwise the product is contaminated with iron. Aluminum, thorium, and titanium are also extracted. The aluminum is not a serious interference, but thorium and titanium build up and require special treatment (stripping with hydrofluoric acid) to remove them.

The solvent has a capacity of about 14 gm U_3O_8/l but, in practice, loadings beyond 8 gm/l result in decreased extraction efficiency.

Uranium is stripped from the solvent with 10 N hydrochloric acid. The acid is recovered by distillation and the concentrated solution remaining is precipitated with ammonia, magnesia or caustic. Chloride, which is an undesirable contaminant in the product, is obviously a problem, and efficient washing is required.

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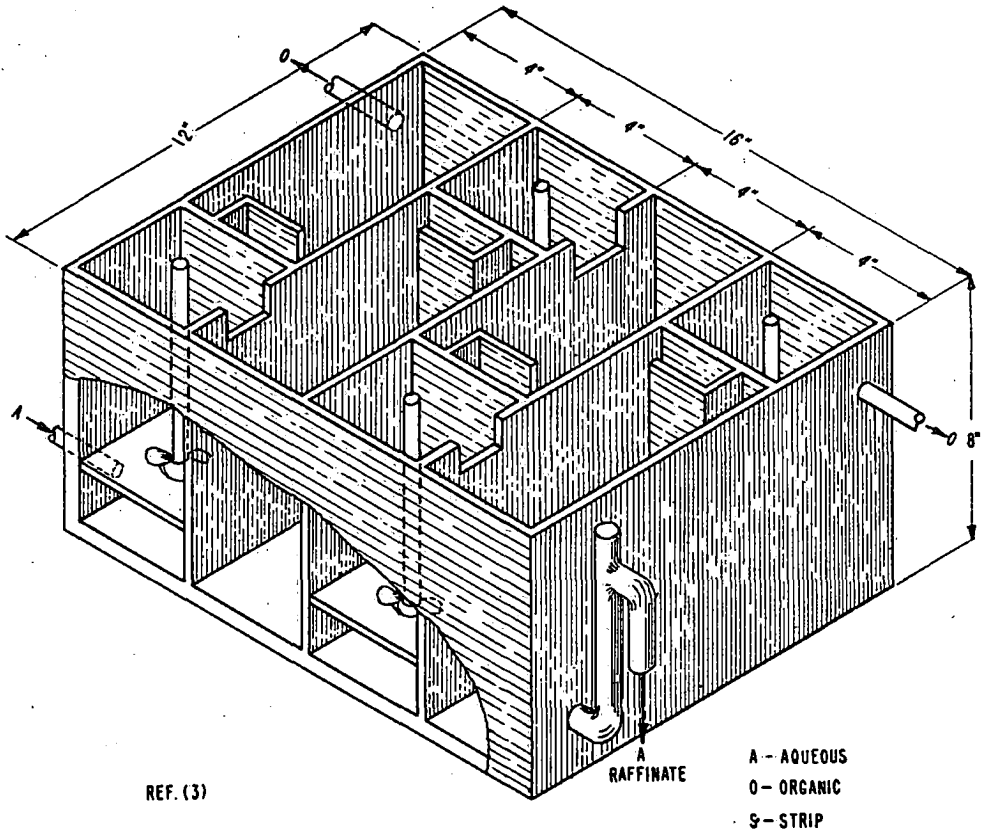

FIG. 2-5 – FOUR STAGE MIXER SETTLER

The Di Alkyl Phosphate Process (28)

This process, which uses a commercially available phosphorus compound, di (2-ethyl-hexyl) phosphoric acid, was developed by the Raw Materials Chemistry Div. of the U.S. Atomic Energy Commission at Oak Ridge, Tenn.

A 0.1 M solution of the ester in kerosene is used as before, and a similar contactor design can be employed. Ferric iron must be reduced to below 1 gm/l.

The reaction is given by

$$2R_2\,P\,(O_3)\,OH + UO_2\,SO_4 \rightleftharpoons UO_2\,[R_2\,P\,(O)_3\,O]_2 + H_2SO_4$$

where R = (2 ethyl-hexyl)

Vanadium, molybdenum, thorium and titanium are also extracted to some extent, generally being partly displaced as the solvent becomes loaded with uranium. The optimum pH is 1.0, at which value vanadium pick-up is minimized.

The Alkyl Amine Process (29-36)

Amines are, in effect, liquid anion exchangers and in most of their properties behave in a manner strikingly similar to the anion exchange resins used for uranium recovery, which have already been described. There are important differences, however. They are not susceptible to poisoning, and are more

selective than the resin. Both secondary and tertiary amines are used and the respective reactions are illustrated by:

$$2\,(R_2NH_2)_2\,SO_4 + UO_2\,SO_4 \rightleftharpoons (R_2NH_2)_4\,UO_2\,(SO_4)_3$$

$$2\,(R_3NH)_2\,SO_4 + UO_2\,SO_4 \rightleftharpoons (R_3NH)_4\,UO_2\,(SO_4)_3$$

The alkyl groups (R) are long-chain and highly branched, which serves to decrease the solubility of the amine in the aqueous layer. Specific types of branching seem to confer selectivity for uranium extraction.

The amines are more selective for uranium than are the phosphorus compounds. As has been pointed out, they resemble anion exchange resins in many ways and this includes their behaviour to cations other than uranium. Ferrous iron is not extracted and very little ferric iron is taken up so that reduction of the liquor is not necessary. Vanadium is extracted, but vanadium pick-up can be reduced by operating at pH 1.0 or below if necessary. Molybdenum is completely extracted. The thorium distribution coefficient varies with the degree of substitution of the nitrogen of the amine and can be quite low in the case of tertiary amines. On the other hand suitable branching of the alkyl groups can result in enhanced thorium extraction, and some secondary amines are effective for thorium recovery. Selective stripping of thorium is possible (e.g. with dilute phosphate or oxalate, prior to uranium recovery).

Another method of reducing impurity pick-up, common to most of these solvent extraction processes, is by loading the solvent to capacity with uranium. The capacities of 0.1 M amine solutions are in the range 4 to 6 gm/l U_3O_8 and saturation loading is accomplished by increasing the number of extraction stages. The number of stages required for saturation is a function of the uranium distribution coefficient and is characteristic for each amine. In general, tertiary amines have higher distribution coefficients than secondary amines, which means that fewer stages are required for saturation.

Extraction by amines is possible with solutions which cannot be treated by anion exchange due to the presence of other anions. Thus arsenate, phosphate, polythionates, and fluoride, to name a few, do not prevent extraction and are not carried into the product. Nitrate and chloride however, do interfere, and this point is covered in the section on stripping.

Stripping

The amines present a wide choice of stripping reagents. Nitrate, chloride, bisulphate, sulphate and carbonate systems have been proposed. Magnesia, and lime slurries have also been investigated. Difficulties due to solvent entrainment have so far not been overcome in the case of the last two. Nitrate and chloride solutions strip well, but impurities such as iron, titanium, and thorium are also stripped. In addition, use of these reagents leaves the amine in the nitrate or chloride form, which is not suitable for recycling. It must first be converted to the free-base form with carbonate or hydroxide solution. This involves another step and further reagent cost.

Stripping with carbonate, on the other hand, effects a separation of iron, titanium and some of the thorium. These are stripped, but their carbonates are insoluble (thorium carbonate is partly soluble). There is some mechanical difficulty due to accumulation of precipitate at the solvent-strip solution interface but this can be overcome. The carbonate strip leaves the amine in the free-base form, ready for use, although in practice a sulphating treatment may be desirable, to prevent a rise in pH when the recycled amine contacts the leach liquor.

The bisulphate strip solution, as might be expected, does not have a very favourable distribution coefficient so far as stripping is concerned and has not been investigated very thoroughly.

The ability of sodium sulphate solutions at pH 4.0 to 5.0 to strip tertiary amines, has recently been discovered (33). Although the sulphate system has not been fully evaluated, it appears that the distribution between organic and aqueous phases is quite satisfactory and favours uranium over impurities, so that the product is purer than with the other systems. The amine is left substantially in the free-base form and can be recycled directly or after a wash with 5% sulphuric acid to convert it to the sulphate form. An important advantage of this method of stripping is that the product can be precipitated free of chloride or nitrate so that excessive washing is not required. It is also probably the cheapest stripping procedure available.

Precipitation from Strip Solution

Precipitation is relatively simple. In the case of magnesia slurry stripping, the product is obtained as a precipitate, needing only to be filtered. The nitrate, chloride, bisulphate and sulphate systems require only that the pH be raised to 7 to bring about precipitation, and the same reagents can be used as were noted in connection with the precipitation from ion exchange solutions. The concentration of the reagents in the strip solution may require adjustment after precipitation, and the build-up of sulphate in the nitrate and chloride systems must be followed, so that sulphate concentration can be maintained below a harmful level. The volumetric nitrate and chloride methods NO_3–2 and Cl–2 are recommended. These same methods can be used to follow the build-up of nitrate and chloride in the solution used to convert the amine to the free-base form, since such build-up must obviously be controlled. Sulphate concentration is followed by means of the gravimetric method.

The precipitation of uranium from carbonate solution can follow either of two courses. Carbonate can be destroyed with acid, and the uranium precipitated as above, or uranium can be precipitated by caustic as in the carbonate leach method. The latter procedure permits recycling the barren strip solution after recarbonation, and is usually slightly more economical. Carbonate make-up requirements are high, however, owing to the amount of bisulphate ion carried over from the leach liquor. Some provision is required for a bleed of sulphate from the recycled strip solution. Control of the concentrations of the carbonate, bicarbonate and hydroxide in the carbonate system is accomplished using Method CO_3–1.

Precipitation from the sodium sulphate strip solution requires only a small addition of caustic (about $\frac{1}{4}$ the usual amount), since the stripping reaction at pH 4.5 results in formation of $U_2O_5^{++}$, so that hydrolysis is already largely accomplished. This species apparently forms a neutral, soluble sulphate complex.

The solvent extraction processes will probably require considerably less analysis than the ion exchange process and extreme rapidity in obtaining results will not be as important. There is, for example, no breakthrough to catch. After a few hours running, equilibrium conditions exist throughout the circuit and the principle consideration is to see that the various concentrations are maintained at optimum levels

Glossary of Terms Used in Solvent Extraction

Mixer—Chamber for mixing solvent and aqueous phases.

Settler—Chamber for allowing the mixed phases to separate.

Mixer-settler (1 stage)—A unit combining the two.

Loading stage—A mixer-settler or other contactor for handling aqueous feed and solvent.

Stripping stage—A mixer-settler or other contactor for handling solvent and strip solution.

Aqueous feed (pregnant liquor)—The solution from acid leaching adjusted to the proper pH for solvent extraction.

Extractant (solvent)—A liquid organic material insoluble in the aqueous phase, that can extract uranium from low-concentration solutions.

Raffinate—An aqueous phase that has contacted the organic solvent and has had some uranium removed.

Strip solution—An aqueous solution that will remove uranium from the organic phase to provide a high concentration of uranium.

Recycle solvent—Solvent that has been stripped, washed, and returned to loading.

Interface—The plane of contact between organic and aqueous phases.

Emulsion (crud seaweed)—The terms are used loosely to describe various pasty materials containing the two phases plus any solid matter, intimately dispersed, and floating in either phase.

Distribution coefficient (uranium)—The ratio of the concentrations of the uranium in the two phases in contact.

E_o^a for loading—(o = organic phase, a = aqueous phase)

E_a^o for stripping

Entrainment and entrainment loss—Removal of organic solvent in aqueous phase as small discrete droplets which have not coalesced with the bulk of solvent in the settler.

Solubility (of the active material) and solubility loss—Loss due to actual solubility of the active material in the aqueous layer.

Loading capacity (for uranium)—The extent to which the solvent (or the active material in the solvent) absorbs uranium. It is expressed as gm U_3O_8/l.

Organic-aqueous ratio—The volume ratio of the two phases. This usually has an optimum value which is controlled in the mixer to prevent emulsion formation. It is not related to the respective throughput ratios.

Throughput ratio, organic to aqueous—The actual ratios of the two phases moving through the stages. It will be low in the loading stage, high in wash and stripping stages.

Table 2.7

Typical Analysis Required—Solvent Extraction—Amines

Sample	Analysis	Range gm/l	Frequency	Method
Extraction Section				
Pregnant liquor feed	U_3O_8	1-3	3/day	U-4
	S/SO_4	3-15	"	S-1
	Fe^{3+}	2-5	"	Fe-1
	Fe^{2+}	0-1	"	Fe-1
	Th	0-3	1/day	Th-2
	Cl	0-0.5	"	Cl-1
	As + P_2O_5	0.05 and up	"	As-P_2O_5-2
	+ other impurities of interest		"	

Table 2.7—Concluded

Typical Analysis Required—Solvent Extraction—Amines—*Concluded*

Sample	Analysis	Range gm/l	Frequency	Method
Raffinates				
Stages 1, 2, 3, 4	U_3O_8	0.005-3	3/day	U-1 or U-4
Final raffinate	U_3O_8	0.005-0.01	1/day	U-1
	ThO_2	0-3	1/day	Th-2
	Kerosene (or amine)	0.01-0.03	1/day	Ke-1
Solvent	Amine	30-50	1/week	NH_2-1
Recycle solvent	U_3O_8	0.005-0.10	1/day	U-1
Carbonate strip Section				
Recycle carbonate strip	Na_2CO_3	50	3/day	CO_3-1
	$NaHCO_3$	50	3/day	CO_3-1
	S/SO_4	5-30	1/week	S-1
Solvent stage 1	U_3O_8	0.1-1	1/week	U-1
2	U_3O_8	1-3	"	U-4
3	U_3O_8	2-5	"	U-4
4	U_3O_8	3-6	"	U-4
4	S/SO_4	2-3	"	S-1
Loaded strip solution	U_3O_8	15-30	3/day	U-4
	Na_2CO_3	5-20	3/day	CO_3-1
	$NaHCO_3$	40-50	3/day	CO_3-1
	S/SO_4	5-30	1/day	S-1
Barren strip	U_3O_8	0.02-1	3/day	U-1
	Na_2CO_3	50-80	3/day	CO_3-1
	NaOH	3-10	3/day	CO_3-1

Sulphate strip—similar to above, but omitting carbonate assays

The Alkali Carbonate Leach Process

Leaching Chemistry (37-45)

Alkali carbonate leaching is used for the treatment of ores containing amounts of acid-consuming minerals that would render the acid leaching process uneconomic. These minerals have already been discussed under the acid leach process and it will suffice here to note again that ores containing sufficient acid soluble minerals to rule out acid leaching are rare, according to Thunaes (Ref. 44a, paper A Conf. 8/ P/ 2). Even in these cases, carbonate can sometimes be floated off to provide a suitable feed for the acid process. The economics of the two processes vary somewhat with location, owing to transportation costs, but, in general, the carbonate process is more expensive, requires finer grinding of the ore and gives somewhat lower recovery than the acid process. Sulphuric acid is a cheap reagent that can be transported in concentrated form as sulphur. A soluble carbonate content of 1% CO_2 (acid evolution method) is equivalent to about 44.5 lb of sulphuric acid (100%) per ton (based on the reaction $Ca\,CO_3 + H_2SO_4 \longrightarrow Ca\,SO_4 + H_2O + CO_2$) and, in the absence of actual acid consumption tests, this can be used as a rough guide to the probable acid consumption. It is considered that ore containing 4% CO_2 is likely to be unsuitable for acid leaching, unless the uranium content is fairly high.

There are minerals which consume carbonate also, principally the sulphide minerals such as pyrite, chalcopyrite and pyrrhotite. A sulphur content of 1% will consume about 66 lb. of sodium carbonate per ton of ore theoretically, assuming that the bicarbonate formed is not considered as a loss (Equation 5).

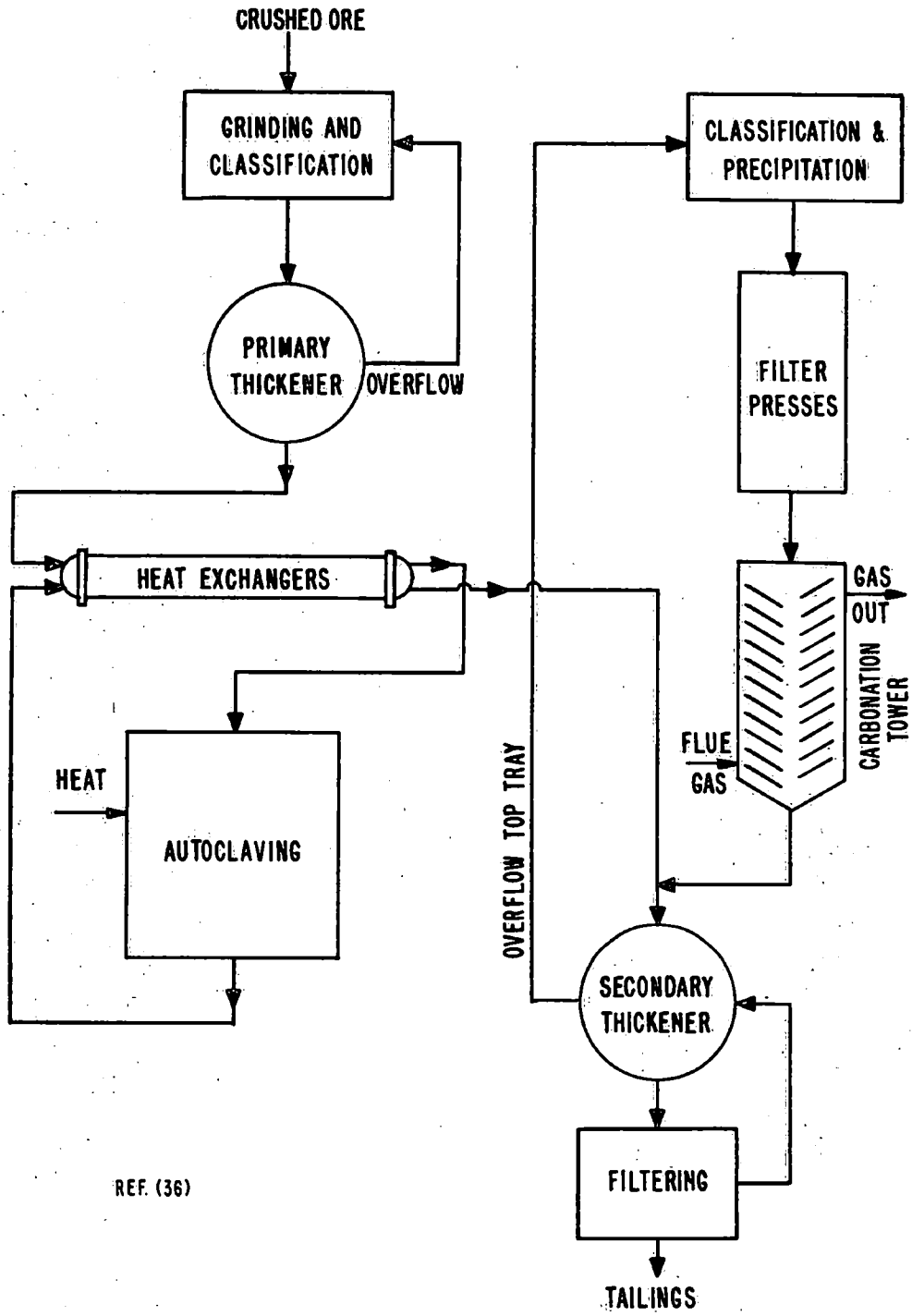

FIG. 26-FLOW SHEET FOR AN ALKALI CARBONATE – PRESSURE LEACH SYSTEM

A sulphur content of 0.5% may be the maximum that can be present for economic carbonate leaching. In practice, all the sulphur present may not react (e.g. Beaverlodge residue contains 0.05% S starting with 0.3% in the head). Nevertheless, at this level some consideration will probably be given to floating off the sulphides and either roasting them, or leaching in a separate acid circuit. Addition of the roasted float to the carbonate circuit will result in some loss of bicarbonate (Equation 10) which can be allowed for in carbonating the barren solution from precipitation.

Graphite is present in many ores and is believed to cause some difficulty with regard to corrosion of mild steel autoclaves. The graphite content can be determined from the difference between the carbonate content by the combustion method (C-2) and the acid evolution method (C-1).

The leach process consists of grinding the ore in 5-7% carbonate solution, thickening and leaching. Leaching is carried out under oxidizing conditions using air or some other suitable oxidant. Reaction rate is increased by increasing the oxidant concentration and temperature. To obtain practical operating rates with air, heat must be used. With air or oxygen as oxidants, the only means for increasing their concentration is to use elevated pressures, due to their insolubility. Thus autoclaves operating at 220°F, 80-90 psi g or pachucas at 160-170°F are used. A pachuca is a tall open tank in which air is introduced at the conical bottom under the pressure of the head of liquid in the tank. Using pachucas, the number of tanks and solution flow rates are adjusted to give a leaching time of about 96 hours. Both air and CO_2 are introduced during leaching. The CO_2 (from flue gas) is scrubbed with water to remove SO_2. The solution must contain sufficient bicarbonate to avoid the formation of insoluble uranates (Equations 2 and 3). Some of this bicarbonate is produced in the liquor on recarbonating the barren liquor from precipitation, usually about 1 to 1.5%. The balance that is required is produced by the reaction of sulphide minerals with carbonate (Equation 5).

The leached ore pulp is cooled by heat exchange with incoming leach feed, and the residue is filtered off.

The clear pregnant liquor is then treated with an approximately 20% NaOH solution, precipitating the uranium (Equations 6 to 7). Control of caustic addition is made by maintaining a definite hydroxide concentration (2–5 gm NaOH/l).

$$U_3O_8 + \tfrac{1}{2}\,O_2 \longrightarrow 3\,UO_3 \qquad (1)$$

$$U_3O_8 + \tfrac{1}{2}\,O_2 + 3\,Na_2CO_3 \longrightarrow \underbrace{Na_4UO_2(CO_3)_3}_{\text{Soluble}} + \underbrace{Na_2U_2O_7}_{\text{Insoluble}} \qquad (2)$$

$$U_3O_8 + \tfrac{1}{2}\,O_2 + 3\,Na_2CO_3 + 6\,NaHCO_3 \longrightarrow 3\,Na_4UO_2(CO_3)_3 + 3\,H_2O \qquad (3)$$

$$NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O \qquad (4)$$

$$4\,FeS_2 + 15\,O_2 + 16\,Na_2CO_3 + 14\,H_2O \longrightarrow 4\,Fe(OH)_3 + 8\,Na_2SO_4 + 16\,NaHCO_3 \qquad (5)$$

$$Na_4UO_2(CO_3)_3 + 4\,NaOH \longrightarrow Na_2UO_4\ (ppt) + 3\,Na_2CO_3 + 2H_2O \qquad (6)$$

$$2\,Na_4UO_2(CO_3)_3 + 6\,NaOH \longrightarrow Na_2U_2O_7\ (ppt) + 6\,Na_2CO_3 + 3\,H_2O \qquad (7)$$

$$2\,NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O \qquad (8)$$

$$Na_2CO_3 + CO_2 + H_2O \longrightarrow 2\,NaHCO_3 \qquad (9)$$

$$CaO + NaHCO_3 \longrightarrow CaCO_3 + Na_2CO_3 + H_2O \qquad (10)$$

A spot check of the uranium content of the barren solution is also made using a rapid, visual carbonate: peroxide procedure. The uranium content of the barren is held at about 0.05 gm U_3O_8/l. No loss of uranium would occur even if this concentration rose, but there is no necessity for carrying a large circulating uranium content.

The barren filtrate goes to a carbonation tower where the excess sodium hydroxide is carbonated with flue gas from the (oil-burning) boiler house of the power plant. The gases (14% CO_2) are first scrubbed with water to remove sulphur dioxide. CO_2 is added to give the maximum bicarbonate possible with the dilute CO_2 air mixture (1.5–2% Na HCO_3). The "available sodium", i.e. the total Na available for carbonate and bicarbonate content, is maintained at 5–7% as Na_2CO_3.

An overall sodium balance may be made. The sodium content of the leached residue in particular is often required, since this represents a loss from the system. The relative proportions of carbonate, bicarbonate and sulphate of the residue can be calculated, based on the known contents in the leach solution prior to filtration. The sulphate and sulphide contents of this residue are also of importance as an indication of the completeness of oxidation of sulphide and a guide to probable carbonate losses. The sulphate content of the leach liquor is followed since there is only a small bleed from the system (the filter cake) and it builds up at a fairly rapid rate. It does not interfere directly in the process except possibly to affect filtering rates. The solubility of sodium sulphate decahydrate is 408 gm/l at 30°C, dropping sharply to 50 gm/l at 0°C, and whenever the saturation concentration is exceeded difficulty may arise due to its precipitation.

Recovery of Uranium from Carbonate Leach Liquors

As with the acid leach system, a number of recovery methods are possible. Several that have been considered are: a) direct precipitation with caustic (the Beaverlodge process), b) precipitation with sodium amalgam,, c) electrolytic reduction using diaphragm cells, d) reduction with hydrogen using nickel catalyst (Forward), and e) Anion exchange (column or resin-in-pulp).

The direct precipitation with caustic has been studied in some detail in this Division (43). It is the only recovery method used at present, and is therefore the only one that will be discussed here. The overall precipitation reaction is given by

$$2\ Na_4\ UO_2\ (CO_3)_3 + 6\ NaOH \rightleftharpoons Na_2\ U_2O_7 + 6\ Na_2\ CO_3 + 3\ H_2O$$

Excess sodium hydroxide is required in amounts directly proportional to the concentration of sodium carbonate in the barren solution. The rate of precipitation and hence the efficiency, is greater the higher the initial uranium content. Reasonable concentrations of sodium sulphate (100-150 gm Na_2SO_4/l)—which builds up in the recycled liquor if sulphides are present in the ore—are beneficial. As already noted the only real limit to sodium sulphate concentration is set by its solubility. Sulphate is determined by Method S-1. Precipitation may be a continuous operation. Sodium hydroxide may be prepared as a concentrated stock solution of about 20–30% NaOH in barren carbonate solution. This solution is pumped to the head of precipitation circuit, which consists of a number of tanks in series. Excess sodium hydroxide concentration is determined by titration (Method CO_3–1) and is controlled by the pumping rate from the stock solution tank. Efficiency of precipitation is determined by filtering a sample from the final tank and determining the uranium content visually using the colour developed by adding peroxide to the carbonate solution.

The sodium diuranate precipitate is filtered out and the barren solution is recarbonated:

$$2\ Na\ OH + CO_2 \longrightarrow Na_2\ CO_3 + H_2O$$

Further carbonation can result in formation of bicarbonate:

$$NaOH + CO_2 \longrightarrow Na\ HCO_3$$

Since the sodium carbonate converted to sulphate by the sulphide in the ore cannot be recovered in this way, it is necessary to add additional sodium carbonate make-up each time. A certain amount of sodium is also lost in the residue.

Table 2.8

Typical Analysis Requirements for Carbonate Leach Plant

Sample	Analysis	Range % or gm/l	Frequency	Method
Mill feed	U_3O_8	0.2-0.4		U-1
	S(total)	0.5	3 per day	S-1
	S/SO_4	0.01		S-1
	CO_2	3-5		
Screen fractions of feed	U_3O_8	0.1-0.8	occasionally	U-1
Leach liquor	U_3O_8	2-4	3 per day	U-4
	Na_2CO_3	50		CO_3-1
	$Na\ HCO_3$	50		CO_3-1
	S/SO_4	25-100		S-1
Barren solution	U_3O_8	0.05-0.15		U-1
	Na_2CO_3	100	3 per day	
	NaOH	1-5		
Residue (filter cake)	U_3O_8	0.01-0.03		U-1
	Na	0.2	3 per day	Na-1
	S total	0.1		S-1
	S/SO_4	0.1-0.2		S-1
Washed residue	U_3O_8	0.01	3 per day	U-1

Table 2.9

Typical Precipitate Composition, Carbonate Leach Process

U_3O_8	70-75%
V_2O_5	1
S/SO_4	1
Cl	0.03-0.07
CO_2	1.8-2.0
Mo	0.004-0.008
P_2O_5	0.005-0.10
B	< .001 to 0.005
Heavy metals (acid sulphide group)	0.05-0.06
H_2O	1-2
Ca	0.2
Fe	0.03
Al	0.01
Na	5

Gravity Concentration

Gravity Mill Samples

These samples—table heads, product, various middling samples, and table tails—result from the use of equipment which can produce: a) a shipping grade concentrate and a rejectable tailing, b) a shipping grade concentrate and a tailing which is not rejectable, but is used as feed to a leaching plant, and c) a preconcentrate for use as feed to a leaching plant and a rejectable tailing.

Case c) can arise where the feed is too low grade to leach directly, or contains reagent-consuming impurities which can be removed by this treatment.

The analyses required are those applying to feed and residue materials from the other processes.

Waste Rock

This sample is the country rock which is removed along with the ore where the ore-bearing formation is less than the mining width. It is discarded without treatment, but is frequently checked to ensure no values are being thrown away.

Flotation Processes

Flotation has not yet been successfully applied industrially to the concentration of the uranium minerals in Canada. It can serve to remove reagent-consuming impurities such as carbonate or sulphides, often producing them in a state where they can be used as reagents elsewhere in the process (e.g. pyrite for use in acid production, carbonate for barren solution neutralization). The analyses required would be those applying to feed materials generally.

Analysis of the Product

Table 2.10 gives a typical product specification. The actual figures may vary from mine to mine. It is seldom necessary to analyze for all these impurities, however, since in many cases there is no possibility of them reaching the levels indicated. Vanadium and thorium are restricted because they tend to carry over into the reactor-grade product at the refinery. The same applies to boron and rare earths which are less likely to contaminate the product, but are much more undesirable. Halogens, including fluoride, are restricted because they cause attack on the stainless-steel refinery plant. The other impurities reduce the efficiency of the refinery process.

The uranium oxide content forms the basis for payment and is therefore required on every lot. The highest attainable accuracy is required here, and agreement within 0.3% absolute is required between vendor and purchaser. Otherwise, a sample of the lot in question is sent for umpire analysis and payment is based on the value (of the two reported previously) closest to the umpire value. It might be pointed out that, statistically, about 23% of the samples may be expected to go to umpire if the average difference between the two assays is as high as 0.2%. An average difference of 0.3% will result in 43% of the samples being sent to the umpire.

The methods given in this manual for determination of uranium in high-grade materials (Methods U-4 and U-5) have standard deviations in the range 0.10 to 0.15. With a proper number of replications, this should give assays close enough to the true value so that only a minimum of the samples need be referred to umpire.

Table 2.10

Typical Product Specification

U_3O_8	50% minimum					
V_2O_5	less than 2	parts per 100	parts	U_3O_8		
PO_4	"	" 2	"	"	"	
Mo	"	" 0.6	"	"	"	
B	"	" 0.03	"	"	"	
ThO_2	"	" 2.0	"	"	"	
Cl, Br, I,	"	" 0.1	"	"	"	
F	"	" 0.1	"	"	"	
Cu	"	" 1.7	"	"	"	
As	"	" 0.8	"	"	"	
Co_3	"	" 1	"	"	"	
NH_3	"	" 0.01	"	"	"	
Rare earth oxides	"	" 0.2	"	"	"	

H_2O — Maximum 10% natural weight basis

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Chapter 3

SAMPLING

GENERAL CONSIDERATIONS

The purpose of sampling is to obtain, in the final portion taken for analysis, all the components distributed in exactly the same proportions as in the bulk of the material sampled. This is not possible to do, and the best that can be hoped for is that the sample obtained will approach this ideal. In practice, it will do so to a greater or lesser extent in any particular case, and the frequency with which the sample approaches the ideal will be governed by statistical considerations. In fact, a good deal of practical statistical work has been directed to determining how accurately a sample may be expected to represent the material sampled.

This theory, however, is predicted on the sample being properly taken, since the calculations of the various tables used are based on some form of normal distribution. That is to say, it is assumed that the method of sampling used will be just as likely to give high results as low ones. To ensure that this is so, it is necessary that at each point where the sample is reduced in size (i.e. where a small part of the material is retained as a sample and the balance is allowed to continue through the process), each particle that makes it up shall have an equal chance of remaining with the sample or continuing with the balance of the material. Furthermore it is essential that at no point in the process is there a possibility of the sample being "salted" (i.e. contaminated) with extraneous material. If either of these conditions is not met, the sampling will be biased, and will tend to give values which centre around some value other than the true assay of the material. These values may display a normal distribution around a higher or lower value than the true one, but are more likely to exhibit some kind of skew distribution, making statistical conclusions, even though corrected empirically for bias, unreliable. The possible causes for biased samples will be considered later in this discussion.

A sampling procedure may produce unbiased samples, displaying a normal distribution around the correct value and still not be of very much use, due to the wide deviation of the individual samples from the correct values. This is a situation which can arise in sampling very non-uniform material, particularly if the sample is not crushed sufficiently finely between sampling stages. About the only place it is likely to occur is in custom sample plants dealing with non-homogeneous ores.

In general, the materials which must be sampled with the greatest care are the feed and residue, and the product. Process test work may require careful sampling, but this is usually done on a smaller scale and proportionately more attention can be given to it.

SAMPLING OF ORES AND RESIDUES

Principles

The principles that govern the sampling of uranium ores are the same that apply to other non-metallic ores and excellent treatments of them, both mathematical and non-mathematical, can be found in many reference books (1-4).

The problems are simpler than those met in dealing with metallic minerals such as ores of native copper, gold, and silver. Except for the greater value of the uranium, the ore characteristics resemble those of many base metal ores. For example the specific gravities of the ore minerals, and their ratios to those of the country rock, are similar to those of many minerals of nickel, copper, lead, zinc and even iron. Also like these minerals, they tend to crush more easily than the host rock, so that the values tend to be found in the smaller mesh sizes on crushing. This leads to segregation whenever the material is handled or transported.

The precautions for avoiding the errors likely to arise in sampling minerals with these characteristics are therefore well worked out and can be found in the references. A brief outline is given here indicating the considerations which must be taken into account in deciding on a suitable sampling procedure to handle a particular material.

There are two types of sampling used—hand sampling and machine sampling. Hand sampling includes coning and quartering, the alternate shovel method, the split shovel method, riffling, pipe or dip sampling. Machine sampling can be carried out so that part of the stream is sampled all the time or so that the whole of the stream is sampled part of the time. The latter is the recommended method. One has the choice also between machines that take a fixed percentage of the ore and machines that can be adjusted to take any desired cut. Particle size of the ore at the sampling point is an important factor in gauging the proper amount of sample to take, the idea being that a proper sample contains more than some definite number of particles, regardless of size. As a rough guide, Fulton and Sherwood (9) quote an old rule used with gold ores containing 1 to 4 oz. gold per ton:

Table 3.1

Approximate Relation Between Weight of Sample and Size of Ore Particles

Diam. of largest piece, inches	0.04	0.08	0.16	0.32	0.64	1.25	2.50
Min. weight of sample, pounds	0.0625	0.50	4	32	256	2,048	16,348

Naturally if the uranium-bearing mineral is evenly distributed, a smaller sample will do than if it is in the form of scattered high-grade particles. Table 3.2, reproduced through the courtesy of Dr. E. A. Bugbee and John Wiley and Sons Inc. (1), gives a more complete picture of the amount of sample that should be taken for material in any particular size range, based on the ratio of the specific gravities of the richest mineral to the average grade of the ore. With uranium ores, the richest mineral will grade 5 to 50% U_3O_8 and the average grade will be 0.05 to 0.25% U_3O_8 giving a ratio of 1000:1 at the most; with most ores the ratio will be about 50:1. So far as leach residues are concerned, the richest uranium minerals are usually the most easily leached so that while the average grade will be down to 0.005 to 0.01% U_3O_8, any unleached material will tend to be of the refractory, lower grade type. The ratio might be as high as 1000:1. It is probable that gravity tails will present the most difficult sampling problem as far as lack of homogeneity and high grade-low grade ratio is concerned.

The sampling problem in uranium mills using a leaching process is simplified by the fact that the ore must be finely crushed for leaching, and a mechanical method of sampling of the ore (as leach feed) during feeding, and of the leach residue during discharge, can be used. Since most of the mechanical samplers used cut out samples on a time basis, it is important that the feed rate be reasonably constant. Otherwise samples should be collected and cut on a tonnage basis each time the feed rate is changed.

Table 2.3 gives physical data, including specific gravities, which can be used in forming an idea as to the amount of segregation that is likely to occur with a particular type of ore and helps in applying the data of Table 3.2 (weight to be taken in sampling ores) to a specific material. Information as to the ore from the various areas can be found in some of the publications listed in the bibliography at the end of Chapter 2; reference 12 (Griffiths) is particularly valuable in locating the applicable references.

Table 3.2

Weight to be Taken in Sampling Ores*

Specific Gravity of Richest Mineral	Mesh Size	Particle Diam. Inches	Grade of Richest Mineral, Divided by Average Grade			
			10	50	200	600
			Safe Weight in Pounds When *Largest* Particles Are of Size Given in Second Column			
	120	0.0043			0.003	0.010
	100	0.0055	0.0003	0.0018	0.007	0.021
	50	0.0100	0.0017	0.0095	0.039	0.116
5.0	14	0.0364	0.0585	0.319	1.29	3.90
	4	0.145	2.96	16.1	65.5	195
	2	0.338	30.0	163	664	2,000
		0.5	75.9	413	1,680	5,050
		1.0	486	2,650	10,700	32,300
	120	0.0043			0.005	0.015
	100	0.0055	0.0005	0.0027	0.011	0.032
	50	0.0100	0.0026	0.0143	0.058	0.174
7.0	14	0.0364	0.0878	0.479	1.94	5.85
	4	0.145	4.44	24.2	98.3	293
	2	0.338	45.0	245	996	3,000
		0.5	114	620	2,520	7,580
		1.0	729	3,970	16,100	48,500
	120	0.0043	0.0005	0.0027	0.011	0.032
	100	0.0055	0.0010	0.0055	0.022	0.068
	50	0.0100	0.0041	0.0222	0.090	0.272
10.5	14	0.0364	0.148	0.804	3.26	9.83
	4	0.145	7.78	42.4	172	518
	2	0.338	78.8	429	1,740	5,250
		0.5	230	1,250	5,080	15,300

* Ref. (1) p. 51

Blending of Feeds

As has been noted above, a great deal of statistical reasoning has been directed toward establishing the optimum method for carrying out sampling. A case in point is the blending of feeds. Bennet and Franklin (10) discuss this question and give a method for allocating the number of samples that should be taken from each feed stock to arrive at an estimated mean value for the blended feed which will have the lowest variance (i.e. the value will be the most reliable obtainable.)

Briefly, they state that the number of samples taken for each feed should be weighed in direct proportion to the product of the number of particles in the individual feed stock and the standard deviation of the assay (in the individual feed stock) of the element to be controlled in the blend.

Consider a blend, made up of three components, A, B and C, the weight fraction of each being W_A, W_B and W_C (i.e. $W_A + W_B + W_C = 1$). The relative number of particles of each is the ratio of the number of particles in it to the total number in the blend, and this is directly proportional to the weight fraction, W. The relative number of samples to be taken of each, (N), is given by:

$$N_A : N_B : N_C = W_A \sqrt{\text{var. (A)}} : W_B \sqrt{\text{var. (B)}} : W_C \sqrt{\text{var. (C)}}$$

where var. (A) is the variance of (A), and hence $\sqrt{\text{var. (A)}}$ is the standard deviation of (A), (A) being the assay of the desired constituent in feed stock A.

The following example, based on one of theirs, will serve to illustrate the point.

It is desired to control a uranium ore feed at 0.08%, using ores from 4 different stopes having assays of 0.06%, 0.08%, 0.11% and 0.20%. For some other reason (e.g. carbonate content) it is desired that these be represented in the proportion 45:40:10:5 = A:B:C:D. Let us assume that the variances in the estimates of the uranium content are in each case proportional to the amount present (this is not strictly true, but is fairly close for colorimetric and fluorimetric methods in their proper ranges). In any case, this assumption will serve for purposes of demonstration if the reader will remember that the proper figure to use is that of the standard deviation, a quantity which can be readily determined. It should be remembered however, that this standard deviation is a measure of the accuracy with which the true uranium content is known—i.e. it includes the sampling error as well as analytical error. In applying this section therefore, the standard deviation for the uranium content of the feed stocks should be determined for a large number of samples, rather than just by repetitive analysis of a few.

Then the relative number of samples to take in this case will be $N_A : N_B : N_C : N_D = 0.45\sqrt{.06} : 0.40\sqrt{.08} : 0.10\sqrt{.11} : 0.05\sqrt{0.20}$

$= 0.100 : 0.113 : 0.033 : 0.0225$

$\doteq 10 : 11 : 3 : 2.$

i.e. 10 samples of A, 11 samples of B, 3 samples of C and 2 samples of D should be taken.

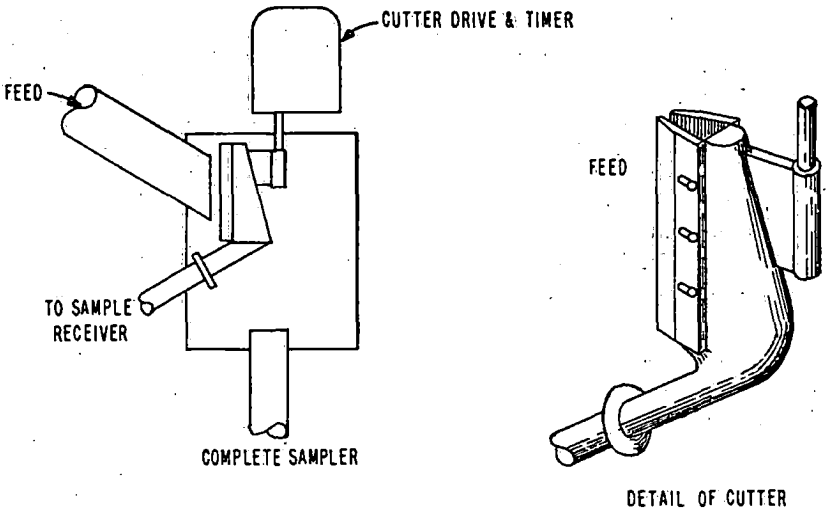
It goes without saying of course, that in the actual blending operation the *weighing* of D should be carried out with the greatest accuracy. It should be fairly obvious however, that the higher the assay, the less error is involved in determining it, which is a qualitative way of putting the above discussion.

Automatic Samplers for Solids and Pulps

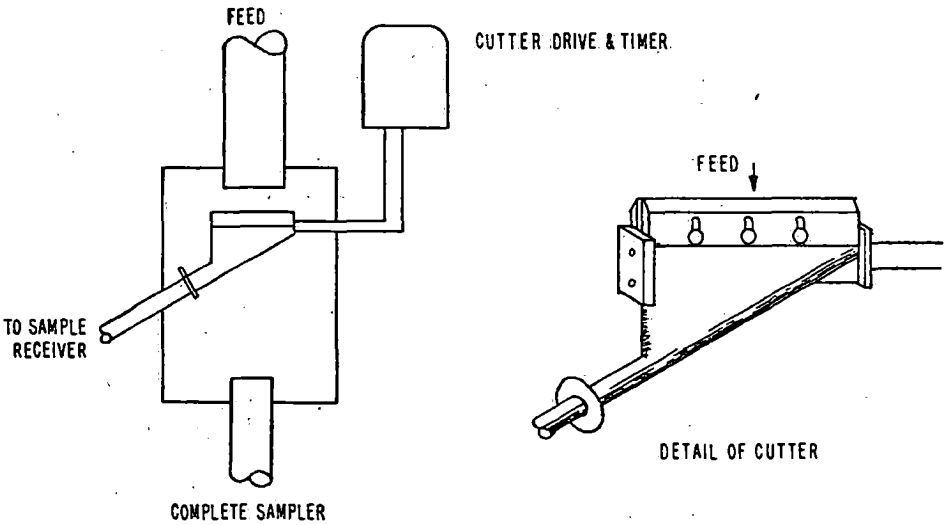
Figures 3.1, 3.2, 3.3, and 3.4 illustrate some types of samplers commonly found in uranium mills.

The Geco Automatic Sampler (Figure 3.1) can be used for wet or dry sampling, and is frequently used to cut pulp samples, e.g. the wet ore pulp feed to leaching and the residue pulp. A gearmotor-driven unit moves the cutter through the stream in a straight line at uniform speed, and the cutter deflects a representative portion of the stream into a separate sample receiver.

In operation, the carrier moves the cutter completely across the stream and stops it. At the end of a fixed time interval, set by means of a controller, the cutter moves back through the stream and stops again for a fixed time. This cycle is repeated indefinitely. The percentage cut can thus be controlled by adjusting the time delay between strokes.



A- VERTICAL SAMPLER (FOR BELTS)



B- HORIZONTAL SAMPLER (FOR CHUTES)

FIG. 3-1 - THE GECO AUTOMATIC SAMPLER.

The Snyder Sampler (Figure 3.2) consists of a circular casting having one or more openings (depending on the percent cut desired) in its sloping flange, and mounted on the end of a horizontal shaft.

The ore to be sampled is directed by a spout so that it falls inside the flange of the sampler. The rejects slide off the flange and continue through the process, while the sample drops into a sample container.

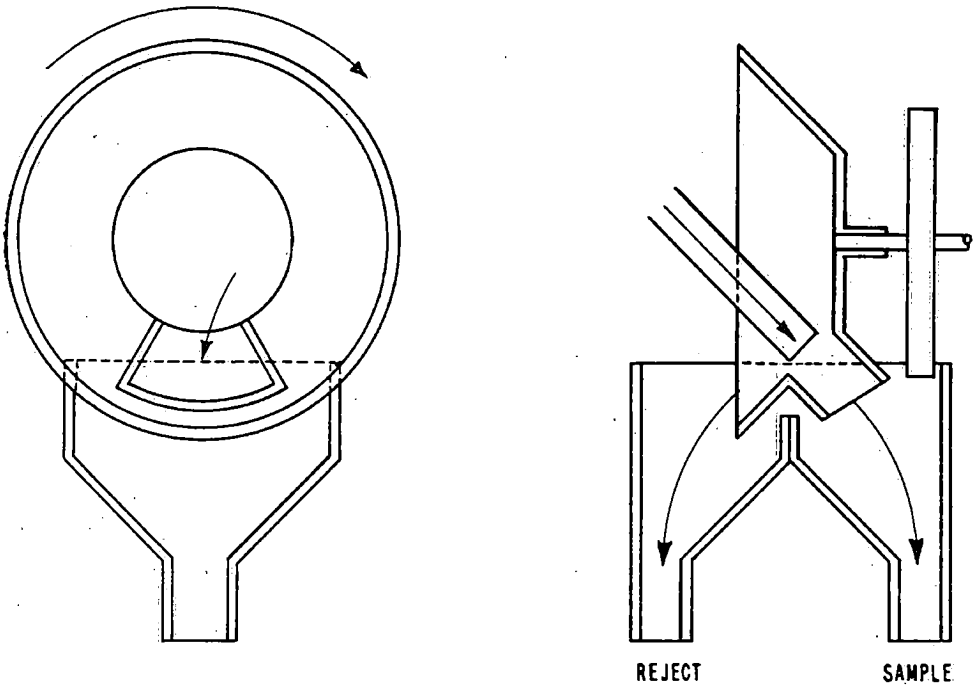


FIG. 3·2 - SNYDER SAMPLER.

This sampler is mostly used for custom sampling of ores. It takes a fixed percentage sample from the ore.

The Vezin Sampler (Figure 3.3) is widely used for sampling concentrates. It consists of a housing within which a cylinder having two or more scoops operates.

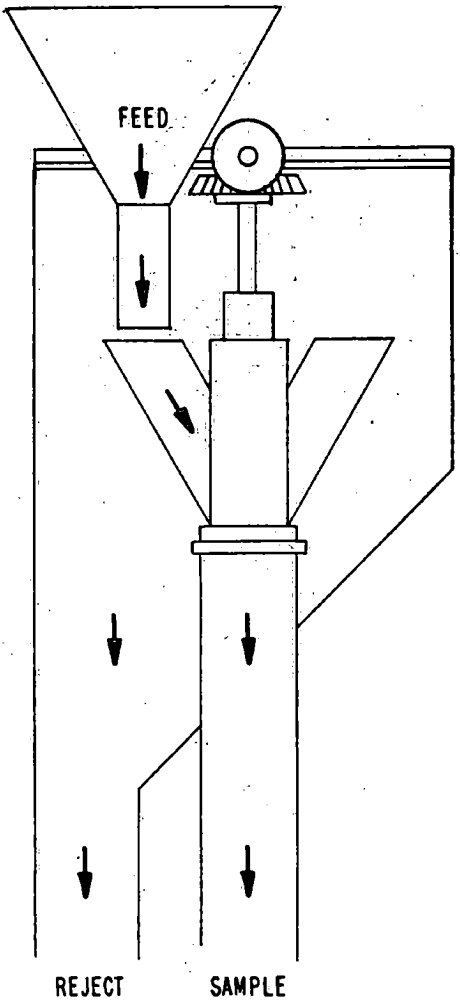
In operation the cylinder and scoops revolve slowly so that the scoops pass under the feed chute and cut out a sample. The sample passes through the cylinder into a sample receiver, while the rejects, in the case of concentrates, drop into the shipping container.

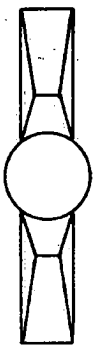
This unit, like the Snyder, cuts out a fixed percentage of the feed.

Continuous Sampler for Pulps (Figure 3.4) is a typical apparatus for sampling pulps, as in feed and residue streams.

Sample Preparation at the Radioactivity Division (Figure 3.5)

Ore (size up to 18″) enters on the first floor and is dumped into a receiving chute. From here it drops into a jaw crusher on the ground floor where it is reduced to $-\frac{3}{4}''$. It then moves via conveyor No. 1 and bucket elevator No. 1 to the second floor where it passes over a $\frac{1}{4}''$ vibrating screen. Fines drop directly onto conveyor No. 3. The oversize moves to a cone crusher on the first floor where it is reduced to $-\frac{1}{4}''$ and drops onto cross-conveyor No. 2 which discharges onto conveyor No. 3 after the fines from the screen.





TOP VIEW OF SAMPLE CUTTER SHOWING SCOOPS AND CYLINDER

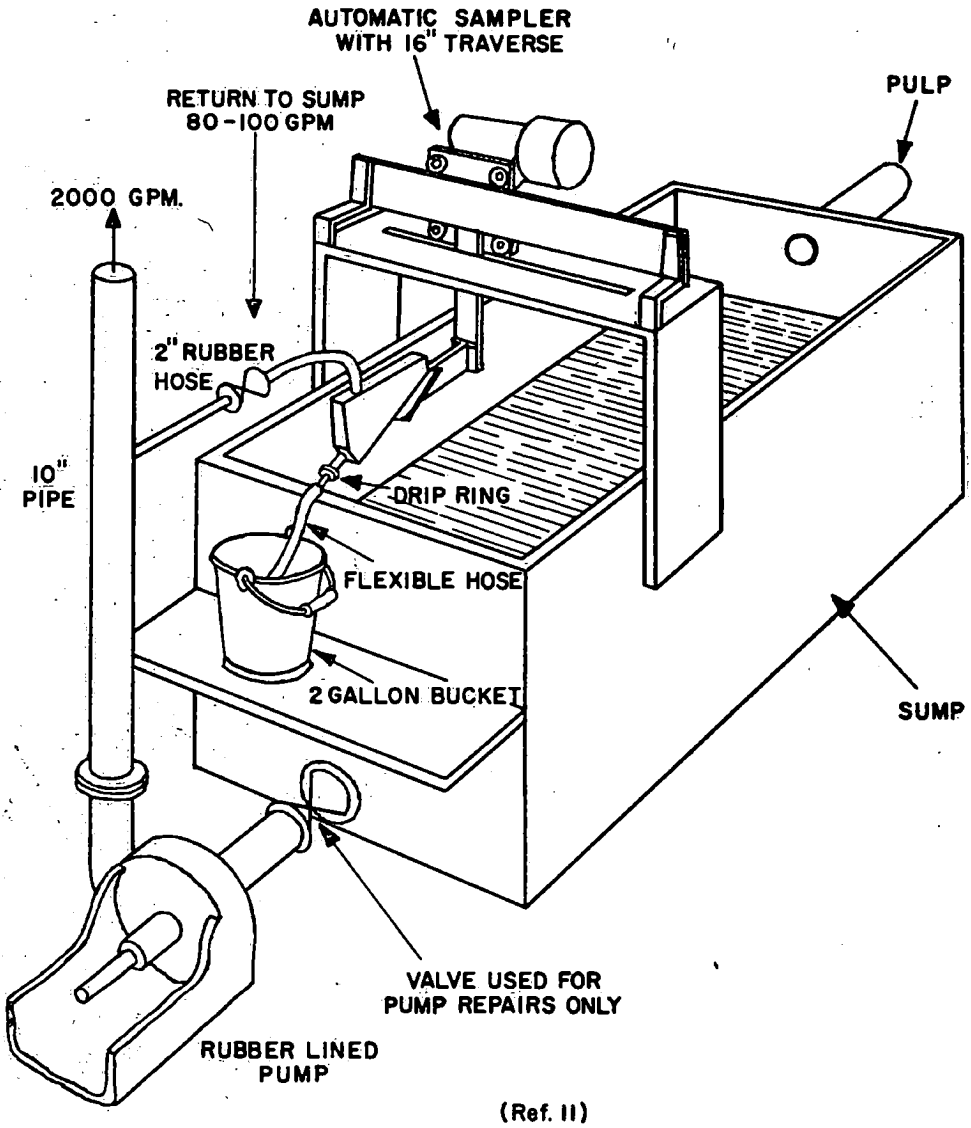
FIG. 3·3 - THE VEZIN SAMPLER

The material, now all $-\frac{1}{4}''$, feeds via bucket elevator No. 2 to the third floor. Here it discharges into a 24″ Snyder sampler, which takes a 10% cut. The reject feeds onto a 16″ belt conveyor into a product bin.

The sample drops into a surge tank and from there goes to a second identical Snyder sample.

The 1% sample, all $-\frac{1}{4}$ mesh, is then riffled down to 0.5 kilograms. This sample is split in two, again using a riffle, and one half is reserved for precious metal assay. The balance of the sample is then pulverized to −100 mesh on a 3 h.p. McCool pulverizer. This sample constitutes the original head sample for the ore.

Figure 3.6 illustrates a typical layout for a sample preparation room, which can be used for handling samples $2\frac{1}{2}''$ diameter and smaller.



(Ref. 11)

FIG. 3-4 - CONTINUOUS SAMPLER FOR PULPS.

For all analytical work, the sample should be –100 and in some cases –150 mesh. For very refractory ores, the samples must be –200 mesh to ensure that it can be decomposed in a reasonable time, and this might as well be done while preparing it. In any case, the same considerations apply with regard to the ratio of grain size to sample taken, in weighing out the sample for assay, as in reducing the ore for sampling purposes in the first place. It is desirable that the grain size of the sample be as uniform as possible and for this reason, the material should be screened frequently during size reduction and the oversize only returned to grinding. The reason for this is that very fine material dusts and segregates readily, and is as undesirable as coarse material.

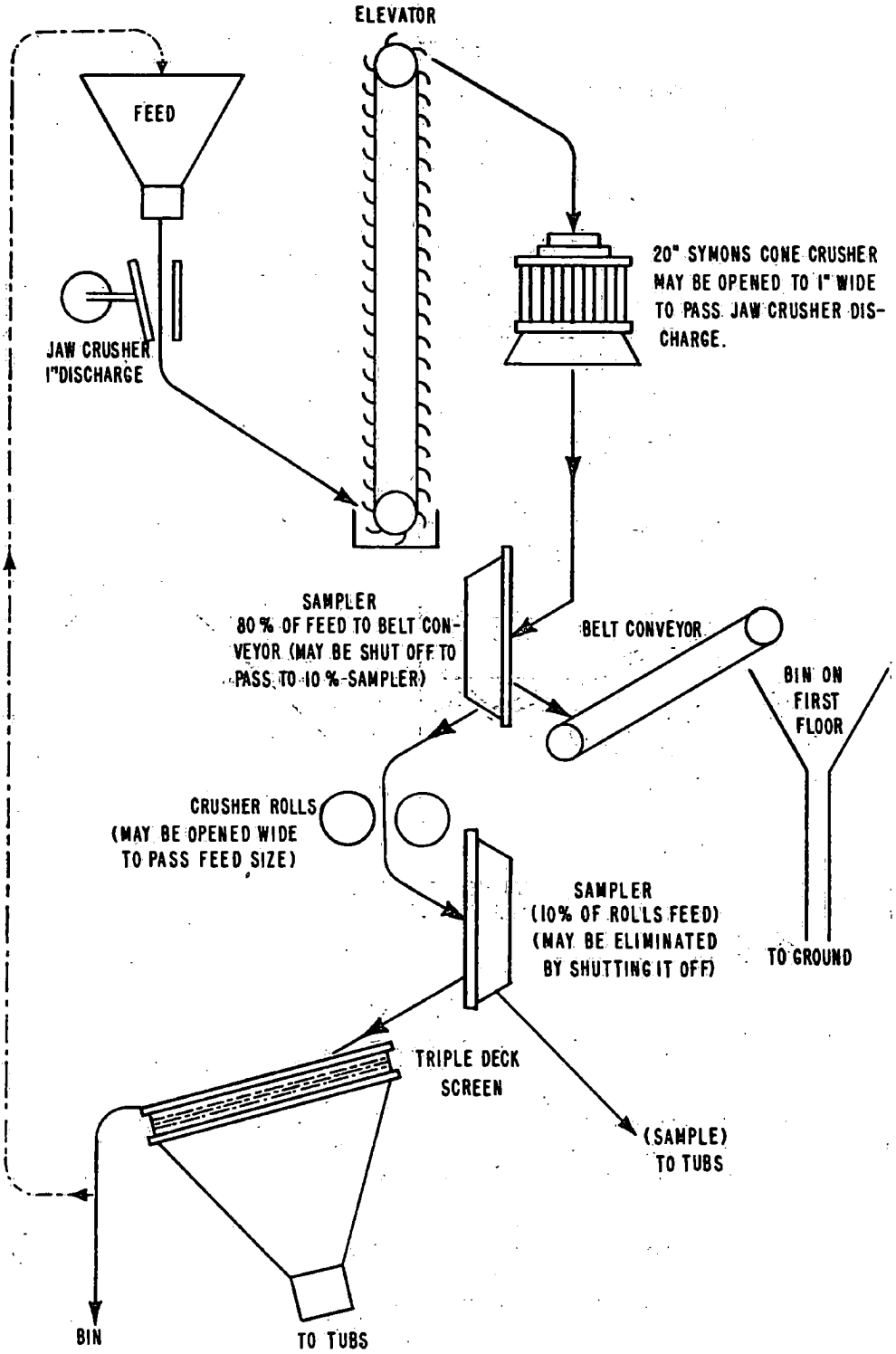


FIG. 3.5 - FLOW SHEET OF MINES BRANCH SAMPLING PLANT

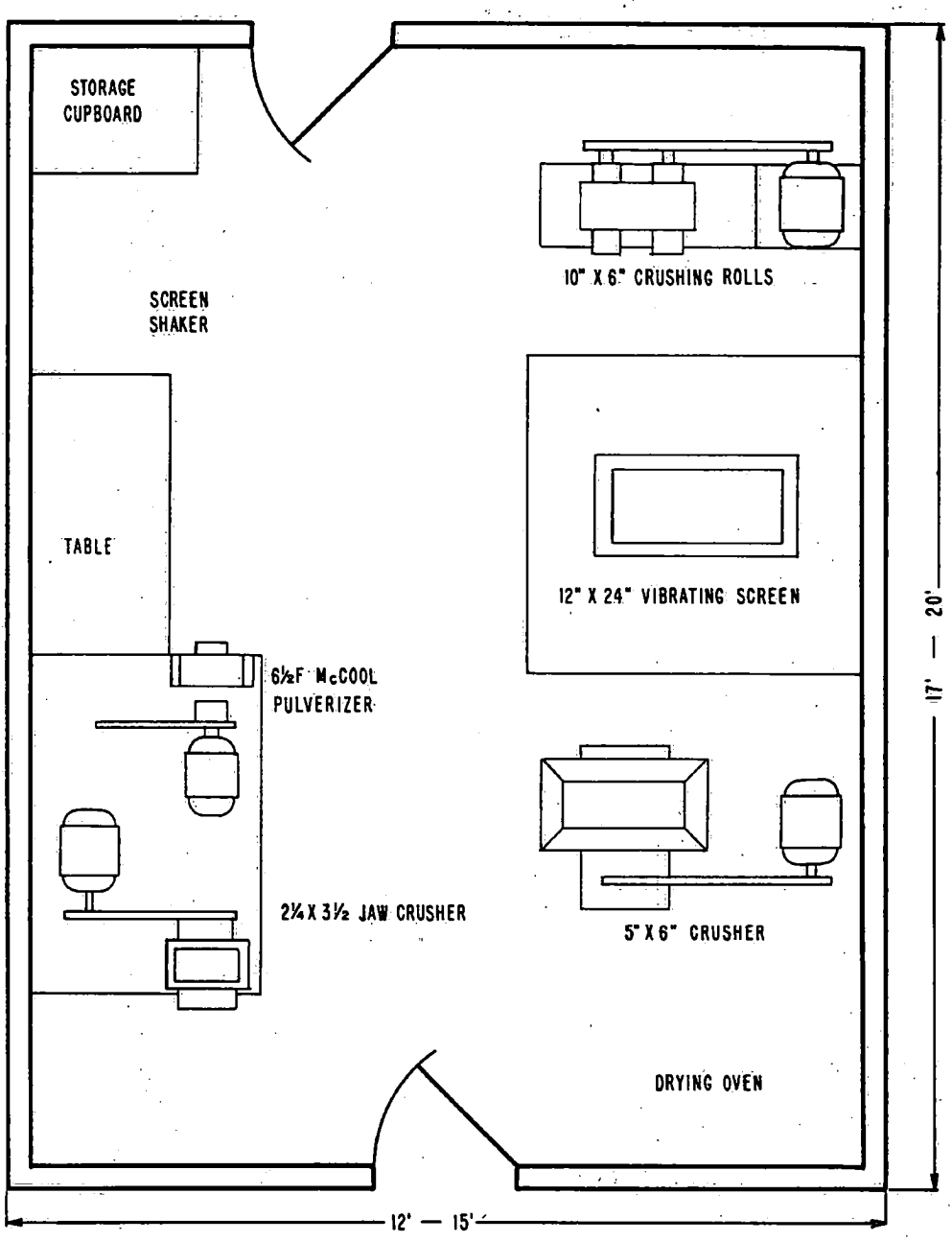


FIG. 3.6- SAMPLE PREPARATION ROOM

REF. (12)

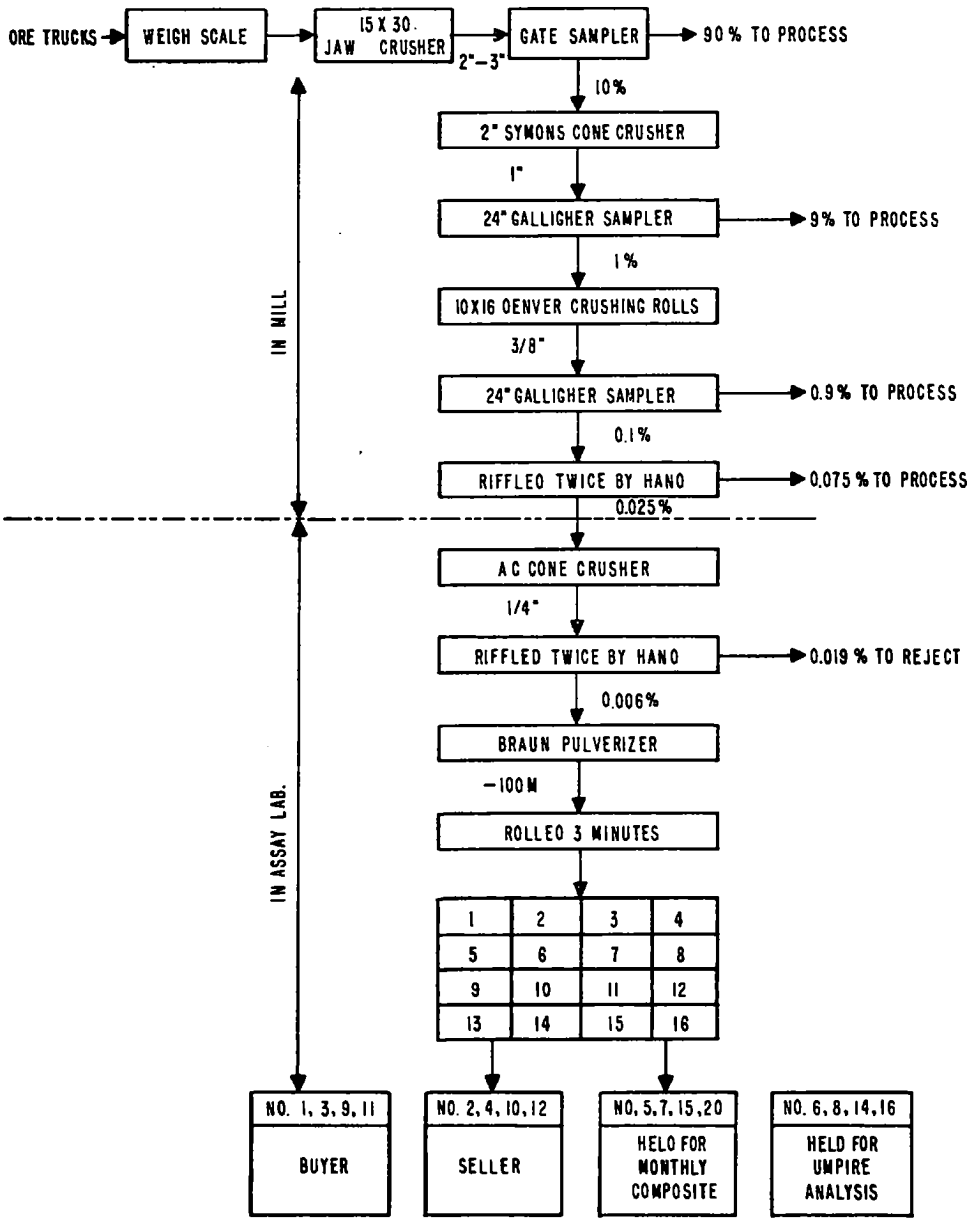


FIG. 3.7 – CUSTOM ORE SAMPLE PLANT FLOW SHEET.

Custom Sampling

Figure 3.7 (courtesy Mr. F. T. Rabbitts, Eldorado Mining and Refining Ltd.) is the flow-sheet for the Beaverlodge custom sampling plant and illustrates a typical uranium sampling plant in operation in Canada.

A brief description of another such plant, at Lorado, will be found in Ref. 8, Ch. 2.

SOLUTION SAMPLING

Solution sampling is somewhat simpler than solid sampling since solutions can be moved (by pumps) and mixed (by stirrers) very readily. Proper mixing is still necessary, since stratification can occur in large tanks, particularly if leachable solid remains on the bottom, or if precipitation is taking place. Such devices as mechanical wet reagent feeders of the cup-type (e.g. the "Clarkson" or "Denver Aerofloat") or adjustable constant-flow pumps can be used to sample solutions continuously in pipes, launders and tanks. Another method is to use a stirred siphoning sump or tank, from which a small sample is mechanically dipped with each filling. If the flow is kept reasonably constant a drip or gravity flow method of sampling can be used. As with solid samples, the sampling rate should be adjusted to the flow rate if this is fluctuating. The sump-type sampler does this automatically.

HIGH-GRADE CONCENTRATES

A variety of methods for sampling this material are available, depending to some extent on the methods used in drying and handling the filter cake up to the packaging step.

At first glance, one would think that any one precipitation batch would be quite uniform in composition, since it is precipitated from a clear solution. However, on reflection it will be realized that precipitation does not necessarily occur all at once. Consider, for example, precipitation by raising the pH. The various elements precipitate successively as the pH is raised (Ref. 17, Ch. 2) in the order, Th^{IV}, Fe^{III}, Zr^{IV}, Sn^{IV}, Sn^{II}, Ce^{IV}, VO^{II}, Cr^{III}, Fe^{II}, Fe^{III}, UO_2^{II}. If a slightly soluble precipitant is used, there will be local high concentrations of hydroxyl ion around the undissolved particle which will nucleate non-homogeneous precipitation. With soluble precipitants, conditions will vary in various parts of the tank due to incomplete mixing and even if mixing is complete, as already pointed out, some elements will precipitate before others. The final product will almost certainly be non-uniform. Furthermore, one would expect that coarse material formed by nucleation around undissolved particles of precipitant would be of different composition than the fine material precipitated in the solution phase.

Differences in physical characteristics, particularly size and density will lead to segregation in handling and packing.

As an example, one mill experienced difficulty in making a metallurgical balance which was traced to discrepancies in the analysis of the product. In this case the product sample was being screened and the oversize discarded, instead of being crushed and combined with the sample. Investigation showed that the coarse material assayed 45% U_3O_8 while the fine material contained 75% U_3O_8. The bias from this practice caused the concentrate to assay 3% high (Rabbitts, F. T., private communication).

If the sample is taken from a stationary container, it should be taken in a systematic manner from all parts of the container. If the container is filled with the wet cake, so that segregation has not had a chance to occur (as for example where the product is dried in trays) it can be sampled according to a scheme similar to that shown in Figure 3.8, equal quantities (of a size to give a total sample containing 0.2% of the total contents) being taken from each of the numbered squares. If the sample is taken from a container which is filled with

1		8		15
	5		12	
2		9		16
	6		13	
3		10		17
	7		14	
4		11		18

FIG. 3·8—SAMPLING SCHEME FOR CONCENTRATES DRIED IN TRAYS

dry, non-homogeneous material, the situation is a little different; if the drum is filled from a hopper, the opening of which is roughly in the centre of the drum during filling, the filled drum resembles to some extent the cone of the well-known "cone and quarter" method of sampling. Figure 3.9 illustrates the segregation which occurs. Here the dotted lines represent successive stages in the filling of the drum. Fine material will tend to stay where it falls, while coarse material will roll down the conical side of the pile and concentrate at the outer edges. In order to obtain a sample truly representative of the drum's contents, a method must be used that approximates quartering, i.e. samples must be taken along radii from the centre to the outside, and correspondingly

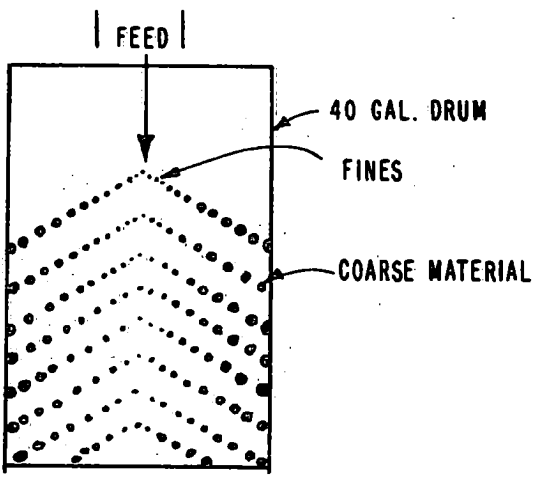


FIG. 3·9—MANNER IN WHICH SEGREGATION CAN OCCUR IN DRUMS DURING FILLING

larger amounts taken from outer edges. Alternatively, the drum may be thoroughly mixed by rotating at a very low speed (5 rpm) using a suitable (end over end) drum mixer, and a single sample taken from a randomly-chosen location in the drum. Simple mixing, even though complete, may not eliminate segregation of the contents of the drum, due to differences in the angle of repose of materials of different size and composition (6), so that a form of quartering may still be desirable. This may be done by taking only one sample per drum, but using a template containing numbered holes to locate the position to be sampled, and drawing up a schedule which favours the outer holes in proportion to the square of the radius from the centre to the sampling position.

In all cases it is assumed that the sampling device samples the complete depth of the drum. An ordinary pipe sampler is not satisfactory due to the tendency of precipitate to pack. The trend therefore is to the use of the auger-type sampler shown in Figure 3.10.

In use, the auger is allowed to drop into the drum (or the drum is slowly raised up to the auger) at such a rate that the auger does not become clogged, i.e. the drum rate of travel is a little slower than the rate at which the auger flights take away the material.

Mechanical sampling of the high-grade precipitate is also common, particularly at the mine mills. A small Vezin sampler is used that takes two 1-lb. samples as the material discharges from the weighing hopper to the shipping drum. Other mechanical samplers may be used (e.g. the Galligher sampler). The important consideration with the Vezin sampler is to ensure that it is turning and that the cutter is not clogged. With the traversing-type of sampler, it is particularly important to make sure it makes the complete traverse since it will cut a sample in any position, but if it does not move, the sample will be a segregated one.

SUMMARY

To sum up, the following are some of the major considerations in sampling and if for any reason the sampling scheme appears to be giving biased samples, the circuit should be checked thoroughly to ensure that these requirements are being met at all the sampling points.

Solid and Solution Samples—All of the stream of material must be sampled, the sample being cut out at intervals. One should never cut a sample from only part of the stream.

Solution Samples—Make sure to purge valves and lines thoroughly when drawing off a sample.

With drip samples, make sure that the drip cock does not become plugged or operate only when line pressure is above some median value.

Sample Preparation—Never discard any material that has not been properly cut out.

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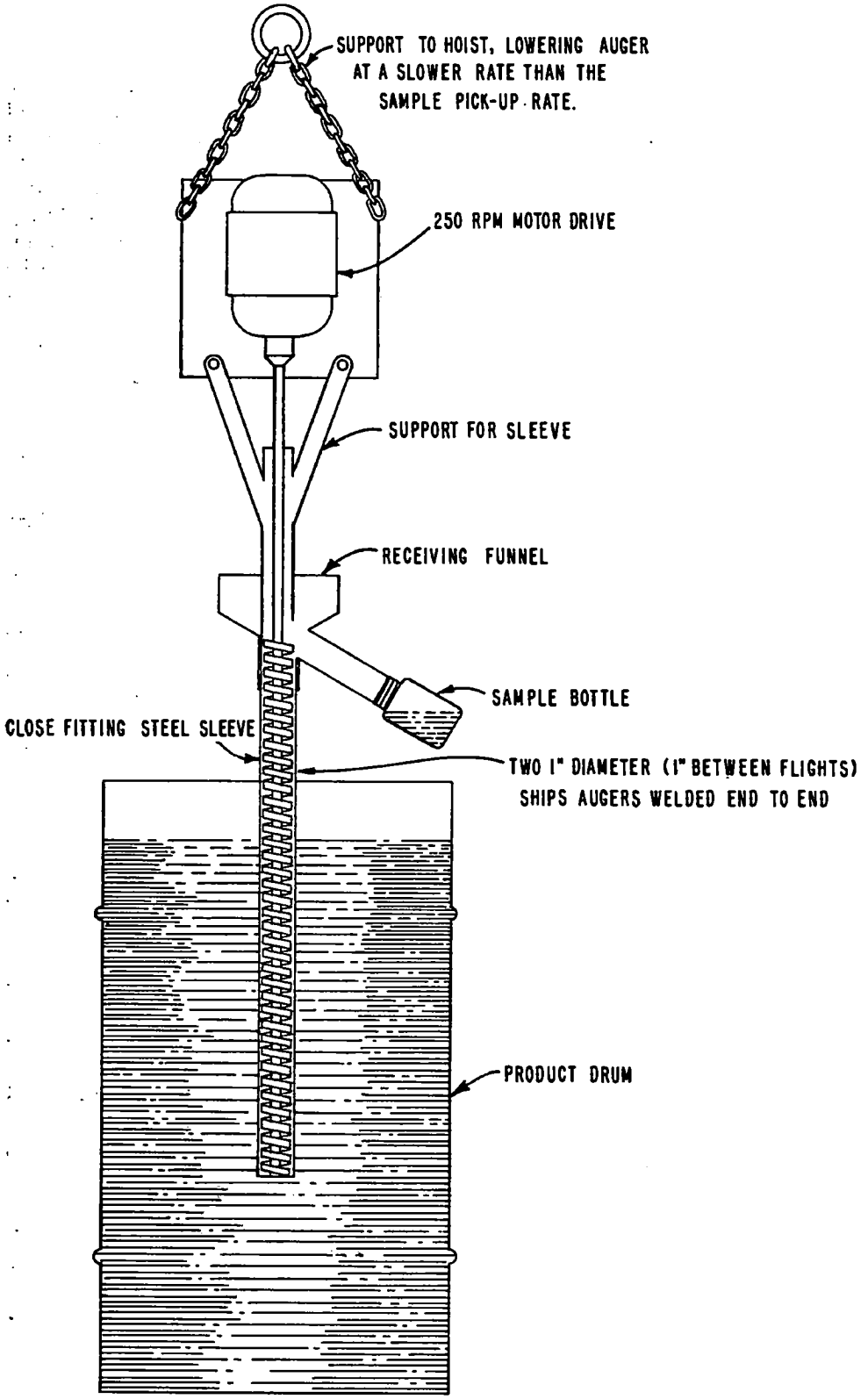

FIG. 3-10 – AUGER SAMPLER

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Chapter 4

COLORIMETRIC THEORY AND THE REDUCTION OF COLORIMETRIC ERRORS

GENERAL

In planning this manual, it was originally intended to include a chapter on errors and statistical methods, and to discuss all types of analytical errors as well as methods for evaluating and reducing them. Unfortunately time did not permit carrying through such an ambitious program. The scope of the chapter has therefore been reduced to a discussion of colorimetric errors. Many of the methods given are colorimetric, and the subject of colorimetric errors has been somewhat neglected in the standard text books, where one usually finds excellent treatments of volumetric and gravimetric errors. Then too, the introduction of differential colorimetric methods requires a knowledge of the error function in regular colorimetry.

The differential method is a means for obtaining a combination of the accuracy of volumetric and gravimetric analysis for higher concentrations, with the selectivity which is the distinguishing attribute of colorimetry. This manual includes such a method (U-4) for the assay of uranium in concentrates with a coefficient of variation of about 0.2%.

REGULAR COLORIMETRY: BEER'S LAW

To understand the basis for this technique, a knowledge of the theoretical background of quantitative colorimetry is required. Briefly, this branch of analysis has as its foundation the law of Bouguer, which states that "each layer of equal thickness absorbs an equal fraction of the light which traverses it", and the law of Beer which states that "the absorbance of a solution is directly proportional to the concentration of the absorbing substance in the solution". The expression combining these two statements is:

$$\frac{I}{I_o} = 10^{-abc}$$

where I_o = the intensity of light incident on the sample
I = the intensity of light transmitted by the sample
a = the absorptivity (*see* following page for definition)
b = the thickness of the solution (i.e. the length of the light path)
c = the concentration of the absorbing substance

The ratio $\frac{I}{I_o}$ is also called the transmittance, designated by t, and $\frac{I}{I_o} \times 100$, called percentage transmittance, is used as one of the scales on most photoelectric colorimeters.

It should be pointed out that Bouguer's law has also been formulated by Lambert, who in addition stated that the amount of monochromatic light

absorbed by a body is proportional to the intensity of the incident light, i.e. the ratio of transmitted and incident light is constant.

The expression may be rendered more useful by taking logarithms of both sides, in which case it simplifies to

$$A = a\ b\ c$$

where A = the absorbance

$$= \log \frac{I_o}{I} = -\log t.$$

$$= \log \frac{1}{t}$$

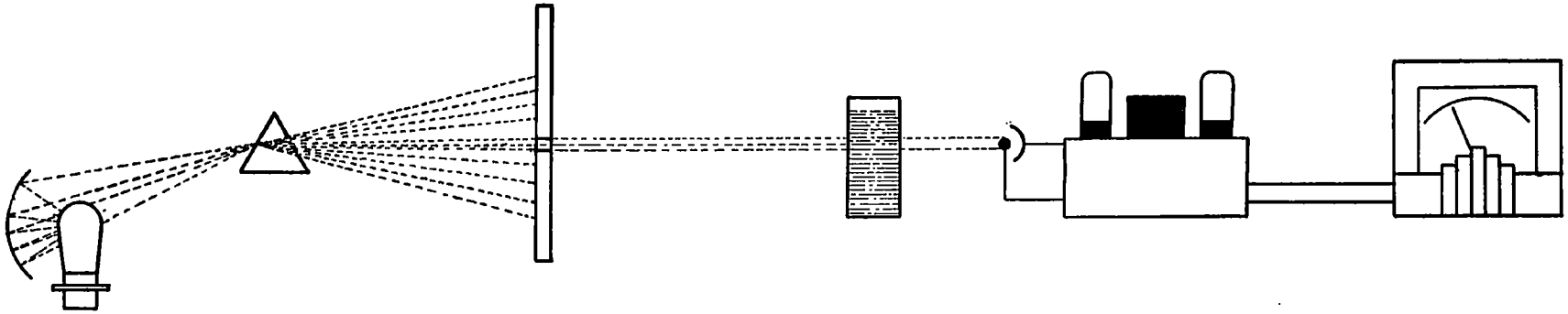
Its utility arises from the fact that it gives us a parameter, the absorbance, which is related linearly to concentration.

The absorbance for unit thickness (path length) and unit concentration of the absorbing substance is known as the absorptivity and can be calculated from measurements on solutions of known concentration.

THE ERROR FUNCTION IN REGULAR COLORIMETRY

Colorimeters and spectrophotometers are basically devices which provide light of a suitable wave length distribution, a place for inserting a transparent container, or cell, of known path length containing the sample solution, and means for comparing the intensity of the light that has passed through this solution with light that has passed through a similar solution that does not contain the absorbing compound. In photoelectric instruments, this comparison is done by means of a photoelectric cell whose output is presented by an electrometric device (Figure 4.1). In the case of the Beckman Model B instrument, a galvanometer is used. The Beckman Model DU uses a potentiometric scale, the scale presenting the value of the current required to balance out the photocell current, as indicated by a null-reading galvanometer. (Figure 4.2)

Such instruments usually measure light intensity on a linear scale, since photocell output is, as a rule, a linear function of light intensity. The result is that the instrument scale is linear with respect to transmittance, since this is actually $\frac{I}{I_o}$ or (in practice), the ratio of the light transmitted by the sample solution to the light transmitted by a reagent blank. To make the instrument more convenient to use, and to simplify the plotting of linear C/A graphs, most manufacturers have also calibrated the scale in optical density (i.e. absorbance), setting off the logarithmic scale from the linear transmission scale. The photocell response is still linear, however. The result of this is that, whereas the error in reading the transmittance scale is constant over the whole scale, this constant error does not apply to the absorbance, or to the concentration which is related to the absorbance in a linear manner. A logarithmic scale becomes continuously more compressed at higher values. Hence ΔA, the error in reading the absorbance or optical density scale, is smaller at lower values where the scale is expanded but where the corresponding concentration is low, and is very high at high values where the scale is exceedingly compressed but which corresponds to high concentrations of the absorbing compound. If we were dealing with a linear scale, having a constant error, the relative error $\frac{\Delta A}{A}$ would be expected to decrease as the absorbancy (and concentration) increased. Instead $\frac{\Delta A}{A}$ is very high at low values, where concentration is low, because A is small. The relative



White light from an incandescent lamp passes through a prism and is spread into its spectrum of colours. The desired wavelength is selected by a knob which rotates the prism, causing the spectrum to move along a slit.

This slit blocks off all but a narrow band of light. Its width is adjustable, allowing any band-width of colour to be chosen. The slit can be made extremely narrow to to give high resolution.

Some of the light rays which enter the sample are absorbed by the coloured compound whose concentration is being determined The others are transmitted through it--------

and strike a phototube. There the light is changed into an extremely small electrical signal. An amplifier then amplifies the signal to provide a measurable meter reading.

This amplified signal positions the needle of an accurate meter to read the exact amount of light passing through the sample The meter scale can be read directly in either transmittance or absorbance.

FIG. 4·1 - HOW A SPECTROPHOTOMETER WORKS.

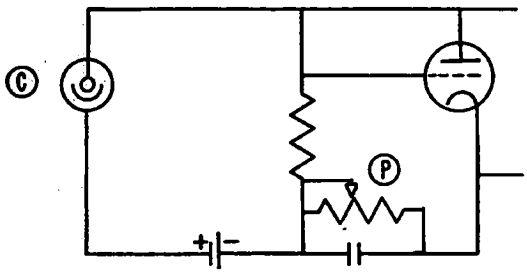


FIG. 4.2—SIMPLIFIED CIRCUIT DIAGRAM TO ILLUSTRATE THE USE OF A POTENTIOMETER (P) IN THE FIRST STAGE OF AN AMPLIFIER FOR MEASUREMENT OF THE CURRENT FROM THE PHOTOCELL (C).

error cannot be reduced, however, (as it would be in volumetric or gravimetric analysis) by using concentrated, i.e. highly coloured, solutions, because while A increases, it does so linearly, while simultaneously ΔA increases very rapidly because the scale is becoming more compressed.

The theoretical curve of the error function for regular colorimetry, whose derivation will be discussed in the ensuing paragraphs, is shown in Figure 4.3 and illustrates this effect graphically. Figure 4.4 is an experimental curve in which the coefficient of variation (a measure of the error function) is plotted against the transmittance ratio in the same way as the theoretical curve. It was obtained from a series of measurements on a group of standard solutions covering the range of transmission readings normally used, over a period of several weeks (ten readings at each transmission value, each reading made on a different day). This curve confirms the theory at least qualitatively.

The question of the error function in regular colorimetry has been dealt with by a number of authorities (1, 2, 3, 4). As we have seen from the preceding discussion, the error function, $\frac{\Delta A}{A}$, is not a simple linear function of A. The following derivation which is necessary for the development of the theory of differential colorimetry, establishes the correct relationship.

Basically, we are attempting to find an expression which will enable us to calculate in absorbance units, for *any* point on the absorbance scale, the magnitude of an interval corresponding to a definite interval on the transmission scale. Then, since the error in reading the transmittance scale is constant over the whole scale, it will be possible to determine the absolute error in the absorbance that can be expected for a particular absorbance reading, and from this, the relative error. Since the fundamental equation involved (Beer's Law) simplifies to $A = -\log_{10} t$ the problem is merely one of differentiating a number with respect to its logarithm.

That is:—

$$\log \frac{I}{I_o} = -abc \text{ . (Beer's Law)}$$

The differential form of this equation is

$$d \log \frac{I}{I_o} = \frac{\log_{10} e \; d\, I/I_o}{I/I_o},$$

$$= \frac{0.4343 \; d\, I/I_o}{I/I_o}.$$

Dividing both sides by $\log I/I_o$ gives

$$\frac{d \log I/I_o}{\log I/I_o} = \frac{0.4343 \; d\, I/I_o}{I/I_o \log I/I_o},$$

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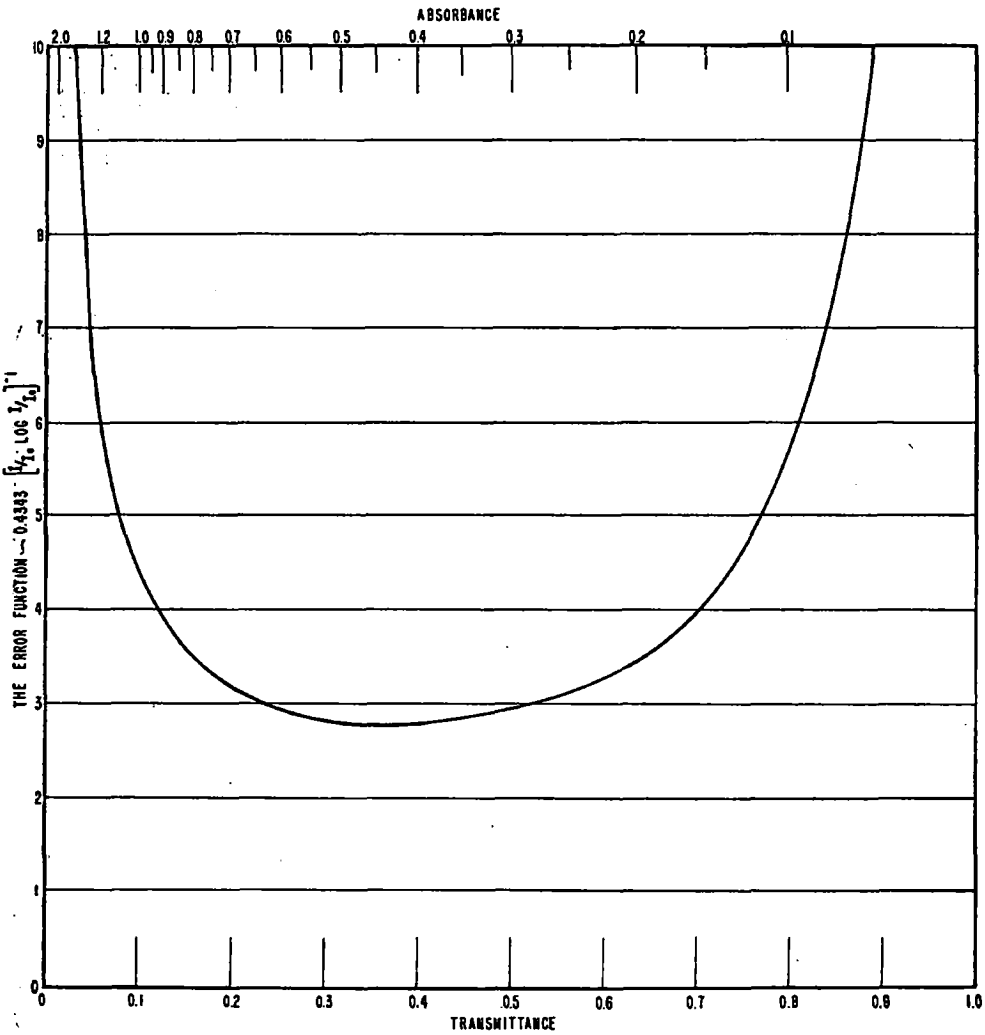

FIG. 4·3 – REGULAR COLORIMETRY, ABSORBANCE ERROR AS A FUNCTION OF READING.

$$\text{i.e. } \frac{dA}{A} = \frac{-0.4343\ dt}{t\ A},$$

where A = absorbance

t = transmission = I/I_o

Or, to derive a similar expression in terms of concentration,

$$d \log \frac{I}{I_o} = \frac{0.4343\ d\ I/I_o}{I/I_o},$$

but $d \log I/I_o = -\ a\ b\ dc$,

so

$$\frac{0.4343\ d\ I/I_o}{I/I_o} = -\ a\ b\ dc.$$

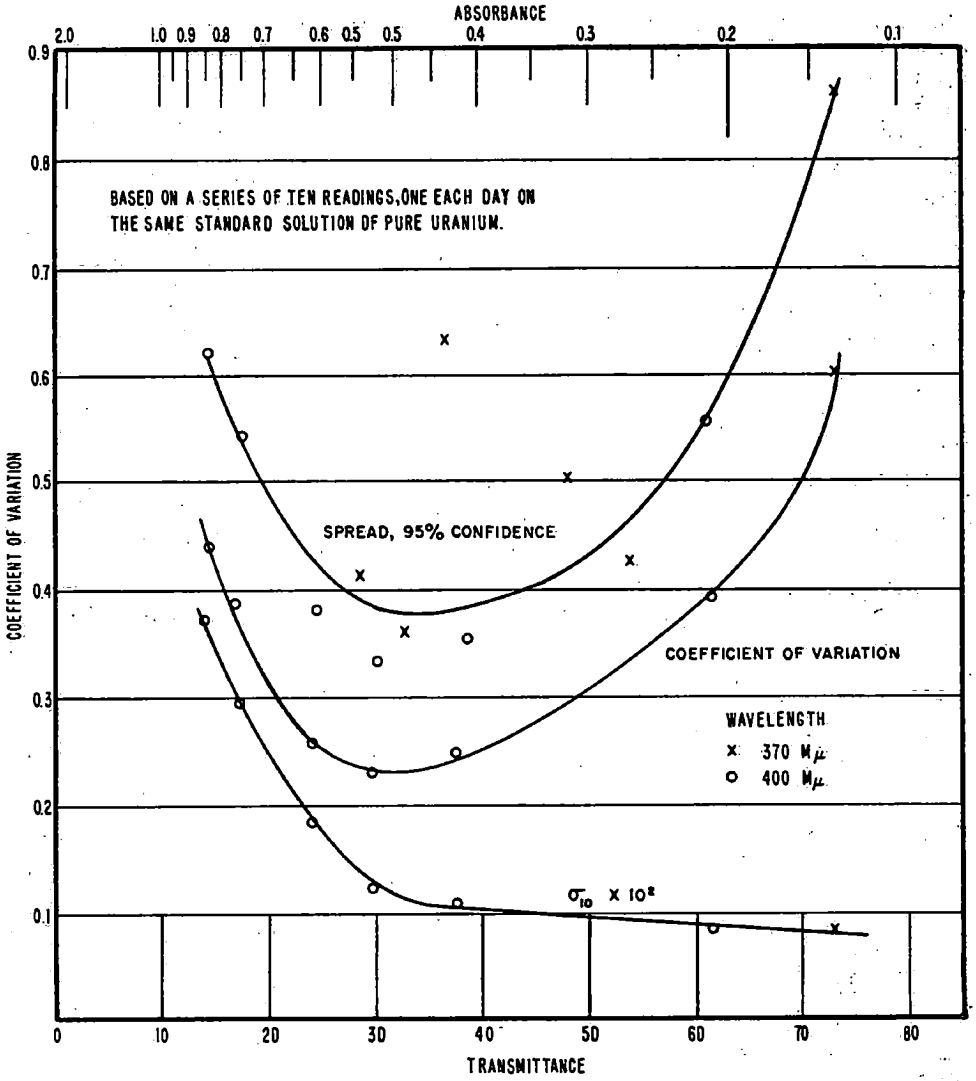

FIG. 4·4 – OBSERVED ERRORS, REGULAR COLORIMETRY.

Since $\log I/I_o = - a\ b\ c$

we can divide the left hand side by $\log I/I_o$ and the right side by $- a\ b\ c$, i.e.

$$\frac{dc}{c} = \frac{0.4343\ d\ I/I_o}{I/I_o \log I/I_o}.$$

Figure 4.3 has been obtained by giving dt the arbitrary value 1% and plotting $\frac{dA}{A}$ against t for various values of t. It is then assumed (2) that if the actual photometric error is evaluated experimentally for a particular instrument by taking a standard solution, measuring its *relative transmittance* repeatedly, and calculating the average deviation, this value can be multiplied by the factor determined from the above expression (or taken from the curve, Figure 4.3) to

obtain the actual photometric error. Furthermore, this relative transmittance error can be used to calculate the error in the optical density at any value. Since optical density is linearly related to concentration, this then is the error in measuring the concentration. Hiskey (3) recommends using the value of twice the average deviation in the transmittance for these calculations.

It may be shown that minimum error occurs when the absorbance has a value of 0.4343, and that absorbances from 0.2 to 0.8 will give reasonable accuracy.

Lothian (Ref. 4, p. 56) has pointed out that the above discussion may be partly vitiated by certain design features of a particular instrument. Gridgeman (5) however shows that it is at least approximately true for the Beckman DU in actual practice (*see* also Figure 4.4).

DIFFERENTIAL COLORIMETRY

The Error Function

Figure 4.6 illustrates three identical spectrophotometer cells, containing respectively, pure solvent (or a reagent blank), a solution containing a coloured compound at a concentration c_1, and a solution containing a coloured compound at concentration c_2. If three beams of light, of identical wave length distribution (in the range where the coloured compound absorbs) and intensity, fall on the cells, the two solutions containing the coloured compound will transmit light which is related to the light passed by the pure solvent by the following equations:

$$I_1 = I_o\, 10^{-abc_1},$$

$$I_2 = I_o\, 10^{-abc_2}$$

The ratio of the light intensities leaving the solutions of concentrations c_2 and c_1 is, then

$$\frac{I_2}{I_1} = \frac{I_o\, 10^{-abc_2}}{I_o\, 10^{-abc_1}},$$

$$= 10^{-ab(c_2 - c_1)}.$$

From this it follows that the transmittance ratio of the solution whose concentration is c_1, based on the pure solvent as 100%, is given by

$$\frac{I_1}{I_o} = 10^{-abc_1},$$

and its absorbance $A_1 = abc_1 = -\log \frac{I_1}{I_o}$.

The transmittance ratio of the solution whose concentration is c_2, based on pure solvent as 100%, is given by

$$\frac{I_2}{I_o} = 10^{-abc_2},$$

and its absorbance $A_2 = abc_2 = -\log \frac{I_2}{I_o}$.

Finally, the transmittance ratio of the solution whose concentration is c_2, based on the solution whose concentration is c_1 as 100%, is given by

$$\frac{I_2}{I_1} = 10^{-ab(c_2 - c_1)}$$

and A'_2, the absorbance of A_2, read against A_1 as 100%, is given by

$$A'_2 = a\,b\,(c_2 - c_1) = -\log \frac{I_2}{I_1}.$$

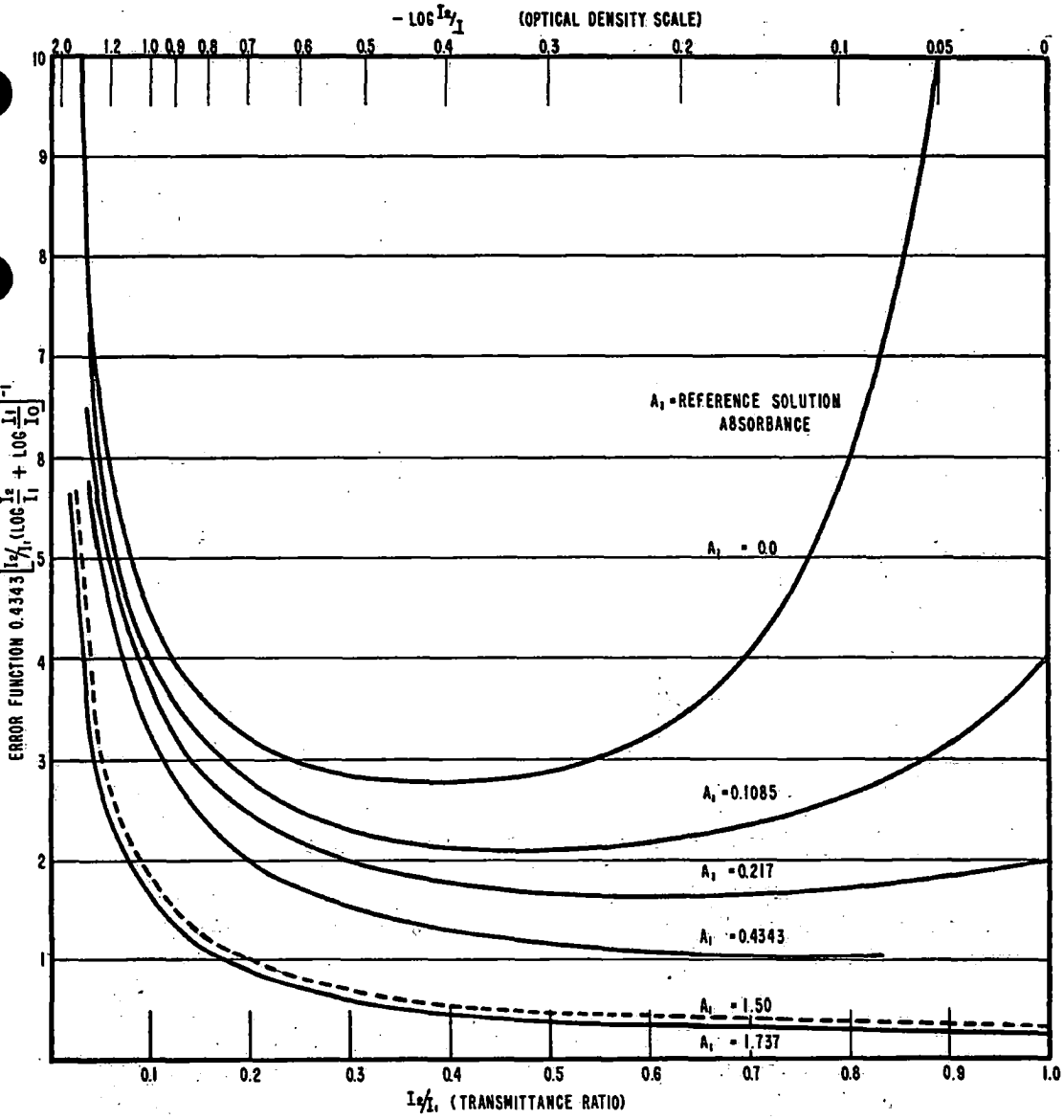

FIG. 4.5—DIFFERENTIAL COLORIMETRY, THE ERROR FUNCTION. (SHOWING ITS DEPENDENCE ON THE TRANSMITTANCE RATIO (I_2/I_1) AND ON ABSORBANCE (A_1) OF THE REFERENCE STANDARD)

In the differential method, we read the intensity of the light transmitted by our sample as a percentage of the light transmitted by a standard having a slightly lower concentration of the absorbing compound we are measuring than does the sample. In other words, we set the transmission scale of the instrument at 100 (as we did with the reagent blank, or water, in the previous case) and read the transmission ratio corresponding to the sample $\frac{I_2}{I_1}$. This is of course,

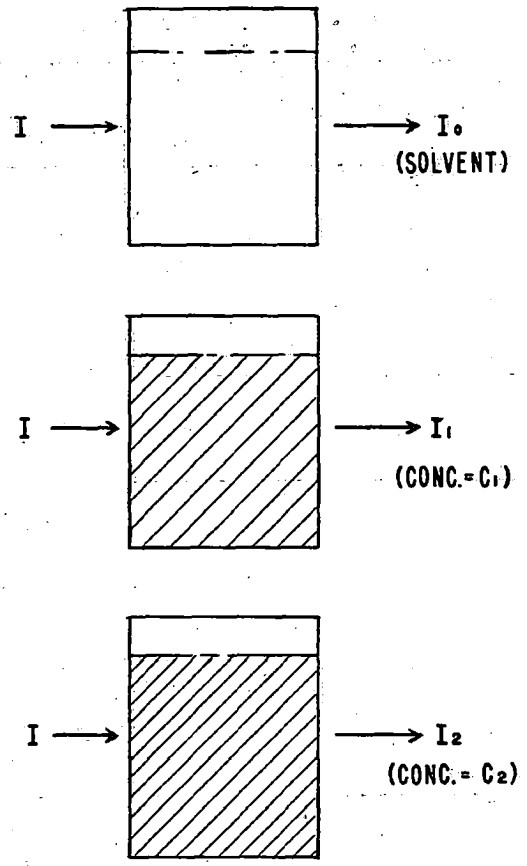

FIG. 4-6—TRANSMITTANCE OF THREE BEAMS OF LIGHT

equivalent to setting the optical density scale of the instrument at zero using the standard, and reading the resulting optical density of the sample A'_2.

$$\text{i.e. } A'_2 = -\log \frac{I_2}{I_1}.$$

Let us assume that there is no deviation from Beer's Law in this higher concentration range, as indeed seems to be the case with the uranium peroxide-hydroxide system, in the concentration range used in the procedure given (U-4).

It therefore follows that, assuming there is no error in preparing the solution at concentration c_2, or in setting A_1, at zero,

since $dA = \frac{0.4343\ d\ I/I_o}{I/I_o}$, the expression for reading error $d\ A'_2$ is given by

$$dA'_2 = \frac{0.4343\ d\ I_2/I_1}{I_2/I_1}.$$

The equivalent error in the concentration measurement corresponding to this absorbance,

$d\ (c_2 - c_1)$, is therefore $\frac{dA'_2}{ab}$,

(since, from Beer's Law), $c = \frac{A}{ab}$.

Since, as noted above, this error in reading $c_2 - c_1$ is in fact the only error involved in determining c_2,

$$d(c_2 - c_1) \equiv dc_2 .$$

The *relative* error in the differential method is therefore given by

$$\frac{d\,(c_2 - c_1)}{c_2} \equiv \frac{dc_2}{c_2} = \frac{\frac{dA'_2}{ab}}{\frac{A_1}{ab} + \frac{A'_2}{ab}} = \frac{dA'_2}{A_1 + A'_2} ,$$

$$\text{but } A_1 = -\log \frac{I_1}{I_o}$$

$$\text{and } A'_2 = -\log \frac{I_2}{I_1}$$

Therefore

$$\frac{dc_2}{c_2} = \frac{\frac{0.4343\ d\ I_2/I_1}{I_2/I_1}}{-(\log I_1/I_o + \log I_2/I_1)} = \frac{0.4343\ d\ I_2/I_1}{I_2/I_1\ (\log I_1/I_o + \log I_2/I_1)}$$

In Figure 4.5 the error function

$$\frac{0.4343\ d(I_2/I_1)}{I_2/I_1\ (\log I_1/I_o + \log I_2/I_1)}$$

has been calculated, assigning a value of 1 for the reading error $d(I_2/I_1)$, and plotted, as ordinate, against transmission ratio (and absorbance) as abscissae. Thus, if the reading error for regular colorimetry for a particular instrument is known, it should be possible to calculate the reading error for differential colorimetry using the factor from this curve.

The curves given are based on reference solutions of various absorbances (A_1) covering a wide range of values. Where A_1 is zero, the curve is identical with that for regular working (Figure 4.6). The value $A_1 = 1.50$ is included because this is the approximate absorbance of the uranium-peroxide colour, for a solution containing 110 mg. U_3O_8 per 250 ml at 410 mμ, which is the reference solution used in the high precision colorimetric method for uranium (METHOD U-4).

The curves illustrate that the accuracy may be increased by increasing A_1, the absorbance of the reference solution, and at values of A_1 above 0.4343 by using a reference solution with an absorbance as close to that of the sample solution as possible. The practical limitation is set by the fact that eventually the solutions employed are so dense that no light can get through to the photocell —for example a solution with an absorbance of 1.737 is only passing 1.8% of the incident light.

It might be well to point out that there is no particular point in using relatively insensitive systems with a view to increasing the concentrations involved, since concentration as such does not enter into the error function. That is to say, increasing c does not decrease the error, dc/c, if dc increases proportionately. Thus it is felt in this laboratory that the hydroxide-peroxide system, which gives a linear Beer's Law relationship and is free from many interferences, is superior to the uranyl sulphate system, which involves many complexes and gives a non-linear relationship as a result of their interaction, and in addition, is subject to a number of interferences. The possibility of further increases in accuracy by using systems showing positive Beer's Law deviation

is something else again, of course. In any case, Reilley and Crawford (7) offer an instrumental method for simulating positive deviation at will.

Cell Transparency Correction

It will be found in practice, that if all the four cells of a set are filled with water, and the absorbance scale set to zero with one of them, the other cells will not read exactly zero, each one possessing more or less colour than the reference cell. The differences can be enough to cause serious error, but are easily corrected, using correction factor f_1, which is readily obtained. One cell is retained as reference cell for all differential work. All the four cells are filled with water and each sample cell is read against the reference cell as zero, noting the absorbance as + or − depending on whether it is above or below zero. These corrections can then be subtracted from all readings made in the respective cell. In practice, however, some time is saved by combining the cell transparency correction with the path length correction as described in the next section.

Cell Path Length Corrections

Another source of error arises from the fact that the two cells under consideration (the reference cell and the sample cell) usually do not have the same distance between the two optical faces. That is, the light traverses a different length of solution in one cell than it does in the other. This error cannot be corrected by simple addition or subtraction except in the case where the concentrations of the solutions in the two cells are the same. It is necessary, therefore, to find a method of correction which will convert the differential reading obtained from the sample solution in the sample cell to the value it would have had if read in the reference cell.

In regular colorimetry, the path length correction is very easily made. From Beer's Law

$A = abc$, where A = absorbance
a = absorptivity (a constant)
b = path length
c = concentration

If we are using a reference cell with a path length b_m, and a sample cell with a path length b_n, both containing solution of the same concentration, c, the respective absorbances will be

$$A_m = ab_mc \text{ and}$$
$$A_n = ab_nc.$$

It is easily seen that the path length ratio of the two cells can be obtained from the ratio of the two absorbance readings:

$$\text{i.e. } \frac{b_m}{b_n} = \frac{A_m}{A_n},$$

and thus the absorbance reading that any solution would give in the reference cell can be calculated from the result obtained in the sample cell, if this ratio has once been determined by reading the absorbance of the same solution in both cells.

$$\text{i.e. } A_m = A_n \cdot \frac{b_m}{b_n}$$
$$= A_n \cdot \frac{A_m}{A_n}$$

In the differential method, correction is complicated by the fact that the error is a function of the total absorbance, and we do not actually measure total absorbance. In the differential colorimetric method for uranium, however, we use a limited number of reference solutions and it is relatively easy to determine their absorbance to a sufficient degree of accuracy once and for all. This value, added to the differential reading, permits the calculation of the true absorbance of any of the sample solutions. From the true absorbance values, the path length corrections can be calculated using the differential readings only, by means of one additional measurement made during the course of the day's analyses.

The expression, used in correcting the differential reading for differences in cell path length between the sample and reference cells, can be derived in the following manner.

Let us call the true absorbance of the reference solution, concentration C_r (read in the reference cell, path length b_0), A_r. Then, if A_s is the differential reading of the sample solution, concentration C_s, against the reference solution as zero (read in a cell with identical path length to the reference cell), the true absorbance of the sample solution will be $A_r + A_s$.

If, instead, we read the sample solution in another cell of different path length b_1, against the same reference solution in the original reference cell, we will obtain a different value for the differential reading. This value, which is the one we wish to correct, we will designate as A_{s1}. The total absorbance in this case will then be $A_r + A_{s1}$.

From the previous discussion, it should be apparent that we can convert this total absorbance to the value it would have had in the reference cell, by multiplying it by the path length ratio of the two cells.

$$\text{i.e. } A_r + A_s = (A_r + A_{s1}) \cdot \frac{b_0}{b_1}$$

The ratio $\frac{b_0}{b_1}$ can be found by determining the absorbance of the reference solution in each of the two cells, using regular colorimetry. It can be determined more accurately by the differential method, however. That is, we can measure the absorbance of the reference solution in the sample cell (path length b_1) against the same solution in the reference cell (path length b_0).

If we refer to this reading as f_2, then the absorbance ratio will be given by

$$\frac{A_r}{A_r + f_2}$$

We can determine A_r itself with sufficient accuracy either

i) by reading it in the reference cell against water as zero, using the 0.1 setting of the Beckman DU spectrophotometer, adding 1.0000 to the absorbance value obtained, or

ii) by extrapolation from the calibration graph used in regular colorimetry at the same wave length.

This absorbance ratio is equal to the path length ratio

$$\text{i.e. } \frac{A_r}{A_r + f_2} = \frac{b_0}{b_1}$$

The corrected *absorbance*, then, is

$$A_r + A_s = (A_r + A_{s1}) \cdot \frac{A_r}{A_r + f_2}$$

Since we actually use only A_s in calculating the assay, it would be preferable to obtain the above expression in terms of A_s

$$A_s = (A_r + A_{s1}) \cdot \left(\frac{A_r}{A_r + f_2}\right) - A_r$$

which simplifies to

$$A_s = \frac{A_r\,(A_{s1} - f_2)}{A_r + f_2}$$

We can further simplify the calculation if we include in the expression the previously discussed cell transparency factor, f_1. This correction is normally applied by simply subtracting it from A_{s1}.

The final expression used in correcting A_{s1}, the observed differential reading, to give A_s, the corrected differential reading, is then

$$A_s = \frac{A_r}{A_r + f_2} \qquad [A_{s1} - (f_1 + f_2)]$$

where A_s = the corrected differential reading of the sample solution

A_{s1} = the differential reading of the sample solution in the sample cell against the reference solution in the reference cell as zero

A_r = the true absorbance of the reference solution

f_2 = the differential reading of the reference solution in the sample cell, against the same solution in the reference cell (cell transparency corrections applied)

$(f_1 + f_2)$ = the sum of the differential reading due to difference in cell transparency and that due to difference in path length.

The ratio $\frac{A_r}{A_r + f_2}$ can be determined by determining f_2 separately. This can be done by first determining $(f_1 + f_2)$, i.e. the differential reading of the reference solution in the sample cell against the same solution in the reference cell. From this, f_1, the cell transparency factor, determined by reading the sample cell filled with water against the reference cell filled with water, is subtracted. This is then combined with A_r, determined as noted above, to give the required ratio. It need be determined only at infrequent intervals, unless the cells are changed.

In this way, it is only necessary to determine the value of $(f_1 + f_2)$ once with each day's batch of analyses, to apply the required correction to A_s.

Temperature Correction

For water, the temperature coefficient of density at 25°C is 1.00026 per °C. If the temperatures of standard and sample are within 2° C of each other, a precision of 0.05% is possible, without applying a temperature correction.

Refractive Index Correction

No correction is needed in the procedure given since there is no detectable difference in refractive index between the standard and sample solutions.

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PART II

Methods—Uranium and Thorium

Contents

PART II—METHODS, URANIUM AND THORIUM

The Determination of Uranium by the Fluorophotometric Method

METHOD U-1

SCOPE

The fluorophotometric method may be used for the determination of uranium in any sample, provided that a standard deviation of approximately ± 5% is accepable. At the Mines Branch the method is reserved for low-grade samples, and for high-grade material when there is insufficient sample for the other methods.

RANGE

The lower limit for quantitative determination is about 1×10^{-9} grams (1 millimicrogram) of U_3O_8. This corresponds to 0.0001 grams per litre for solutions or 0.00025% (based on a 2-gram sample dissolved to give 50 ml of solution) for solids. The lower limit can be decreased if a prior concentration step such as an ethyl acetate extraction is used.

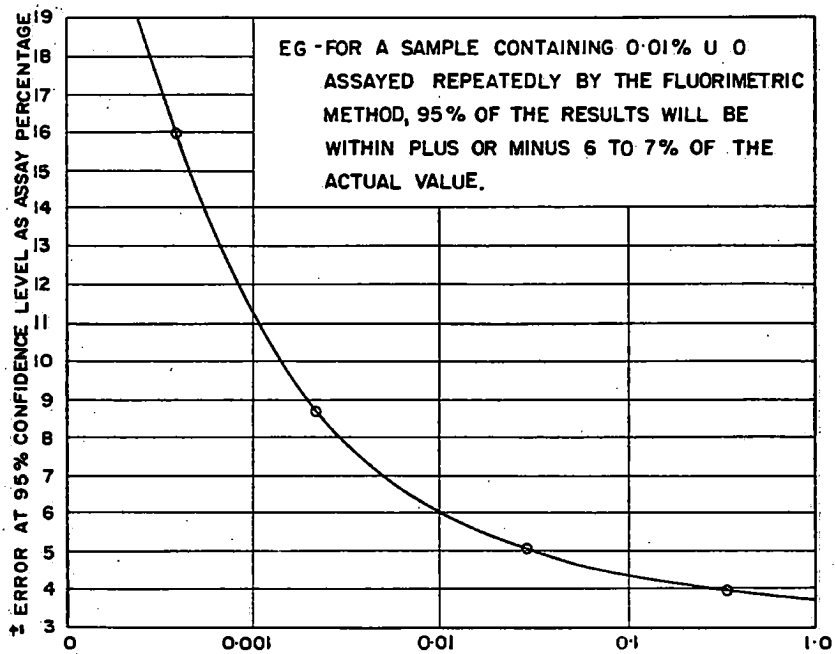


FIGURE 1

ERROR IN FLUORIMETRIC ANALYSIS FOR A SINGLE DETERMINATION CONSISTING OF 4 BEADS

The upper limit has been arbitrarily set at 1% for solids and 1 gm per litre for solutions, since above these concentrations, greater accuracy is possible by the other methods. The error of the fluorophotometric method at various sample concentration ranges is given in Figure 1. This figure is based on the use of the Mohr-type graduated pipette. A substantial increase in accuracy can be expected using micropipettes (± 3% on 2 beads on 0.5% material).

OUTLINE

Fluorescence and Quenching

Uranium fluoresces brilliantly when it is fused into beads of sodium fluoride and is then illuminated with ultra-violet light (1). It behaves similarly with other alkali fluoride and fluoride-carbonate mixtures and with borax, although in each case a different excitation and emission wave length may result. Fluorescence output of beads prepared from pure uranium solutions increases linearly with increasing uranium concentration and can be measured by means of a suitable illuminating and light-detecting apparatus (2, 3, 4).

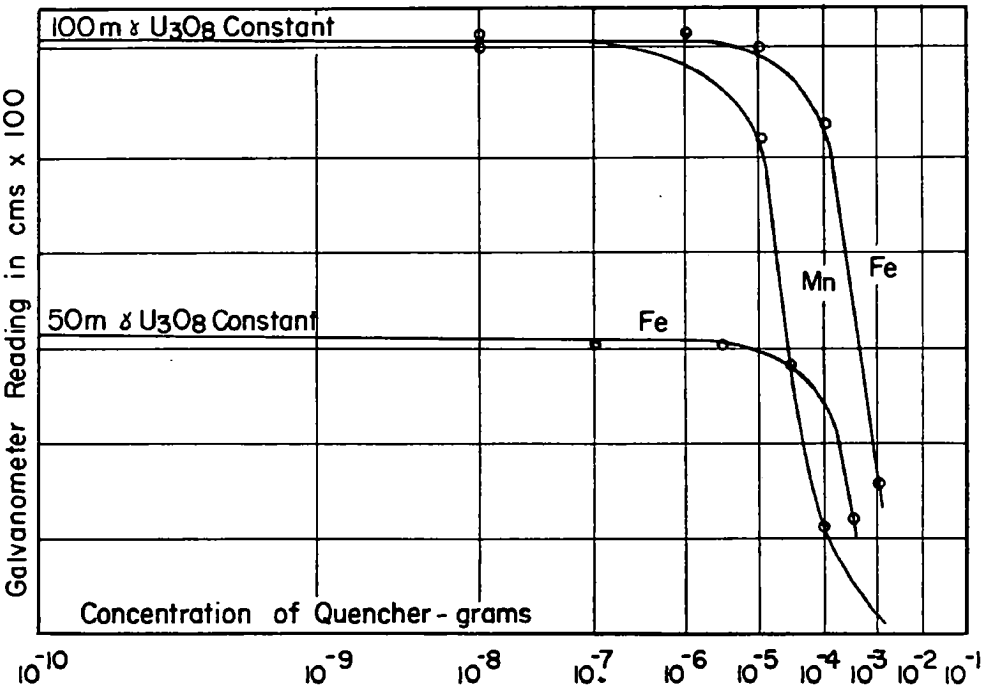


FIG. 2—QUENCHING EFFECTS OF IRON AND MANGANESE

The output of fluorescence is reduced by the presence of excessive quantities of certain interfering elements called quenchers, that produce an effect known as quenching. Figure 2 illustrates the quantitative effect of certain common quenchers. It has been established that the amount of quenching that occurs is a function of the ratio of quencher to flux, rather than of the ratio of quenchers to U_3O_8 (5). Of the various fluxes that may be used, sodium fluoride or the 98:2 sodium fluoride-lithium fluoride mixture recommended by Centanni (12) give the highest sensitivity, and as a result the uranium-containing solution can usually be so diluted that quenchers are without effect. However, minimum error results when the amount of uranium in the bead is in the range 5×10^{-8} grams to 2×10^{-7} grams (i.e. 50 to 200 millimicrograms), using 100 millimicrograms in the standard beads. Above this range, some self-quenching by uranium may occur, and below it, the readings become small enough for instrumental error to become a factor (4). The possibility of quenching is always present and for this reason all samples are determined in the following

procedure by using two different aliquots, one twice the volume of the other. Since the same amount of sodium fluoride is used with both, the quencher-to-flux ratio will be higher in the latter, and if quenching is taking place, the larger aliquot will give a lower reading in relation to its uranium content than the smaller.

If quenching is detected, two alternatives are available; (1) "spiking", and (2) separation of the uranium from the quenchers.

"Spiking" involves the addition of a known amount of a uranium solution containing no quenchers to an aliquot of an unknown sample solution containing quenchers. A second aliquot of the same size containing no added uranium is also taken. The fluorescence of beads prepared from the unspiked and spiked sample solution is then measured. Since the quenching is a function of the quencher-to-flux ratio only, the known amount of uranium will be quenched by the same percentage as the unknown sample and a correction can be made. The formula used to correct a quenched sample by the spiking method is given by

$$\text{millimicrograms } U_3O_8 = \frac{A \times M \times C}{D - A}$$

where A = corrected galvanometer reading of unknown
D = corrected galvanometer reading of spiked unknown
M = corrected galvanometer reading of an amount of pure U_3O_8 equivalent to that added in spiking
C = Calibration constant

However, it will be noted from Figure 2 that the fluorescence drops off very sharply over a relatively narrow quencher concentration range so that the sensitivity of the method is seriously impaired; hence the above technique is used only where samples are already so dilute that the dilution technique is not possible.

The alternative procedure, separation of uranium from quenchers, is therefore preferred for the relatively few cases where it is needed.

The most useful general method is an ethyl acetate extraction of uranium from an aqueous nitric acid solution heavily salted with aluminum nitrate (6, 7). The aluminum nitrate serves both to depress the solubility of uranium in the aqueous layer and also acts as a complexing agent to tie up arsenate, phosphate, fluoride, and sulphate ions, which would otherwise prevent the extraction of all the uranium. Cerium, which interferes by fluorescing at approximately 1% of the fluorescence of a corresponding amount of uranium, must first be reduced to the trivalent form, since the quadrivalent form is extracted by ethyl acetate (7). Hydrogen peroxide is used for this purpose in order not to reduce the uranium. Some thorium is also extracted, but usually not in amounts that will cause quenching. The tributyl phosphate extraction procedure given in METHOD U-3 can also be used.

Ores from Port Radium often contain manganese as the principal quencher (present as the mineral rhodocrosite). This is very conveniently removed by boiling the nitric acid solution with potassium chlorate to precipitate manganese dioxide, which is then filtered off.

$$3\,Mn(NO_3)_2 + KClO_3 + 3\,H_2O \longrightarrow 3\,MnO_2 + KCl + 6\,HNO_3$$

Thorium can be removed by simple precipitation as the fluoride from the nitric acid solution. No loss of uranium has been noted at a ThO_2/U_3O_8 ratio of 200/1.

Some elements that are stated to fluoresce in sodium fluoride are calcium, magnesium, antimony, vanadium, beryllium, molybdenum and niobium (8). Silica, titania and alumina are stated (4) to cause a shift of the fluorescence to lower wave lengths, and hence a reduction in fluorescence as measured by the standard photo tube-filter combination. In the case of niobium, it is best removed by hydrolytic precipitation. Ores containing niobium are usually refractory and are normally decomposed with sodium peroxide. However, peroxide reacts with niobium and prevents its precipitation. Therefore with high niobium-content ores, the sample is first decomposed by means of a pyrosulphate fusion. The other interfering elements noted are easily removed by ethyl acetate extraction. They are seldom found in amounts sufficient to cause interference, with most of the ores treated in this country.

"Brown Bead" Effect (2)

Pink or brown-tinged beads that show marked quenching are produced by fusion in oxidizing atmospheres. The effect sometimes occurs at the edges of the burner or when too hot a flame is used. With some lots of sodium fluoride, the standards have been quenched to a greater extent than the samples, giving high results (and detected by the abnormally low fluorescence of the standards). The effect, which is apparently due to solution of platinum in the bead, is overcome by grouping the beads in the centre of the burner to provide a thick layer of burned gas between the beads and the air, and by cooling the beads in an atmosphere of steam after the fusion. Prolonged use of a very hot flame is also avoided.

Contamination

The extreme sensitivity of this method results in very minute amounts of uranium being present in the final aliquot taken for analysis. For this reason the method is extremely susceptible to variations caused by contamination with uranium ("salting"). High and variable blanks, and erratic results generally, are symptomatic of this condition. It can be corrected by scrupulous cleanliness and by prevention of traffic from the mill into the laboratory.

THE FLUORIMETER LABORATORY

Floor Plan

Figure 3 is the floor plan of a suitable laboratory for pipetting, fusing and reading of phosphors (beads). It is divided into two parts, one of which is reserved for the instrument and must be air conditioned (by a 5 h.p. unit) to provide suitable dehumidification if the M.I.T. instrument is used. The GM fluorimeter does not require this. The other section must be supplied with an ample (500 cu ft/min) supply of tempered, filtered air to replace that withdrawn by the fusion and pelleting hoods. Because of the sensitivity of the method, this room must be adequately protected against the infiltration of dust-bearing air especially if the fluorometric laboratory is situated in an ore-dressing mill. For example, doors should be tight fitting and ventilating openings fitted with glass-fibre filters which should be replaced frequently. The room air supply should give a slight positive pressure in the room.

Fume Hoods

A standard commercial 4-foot hood, lined with fire-brick (and fitted with a suitable flame baffle consisting of 2 sheets of heavy $\frac{1}{4}$-inch mesh wire screening

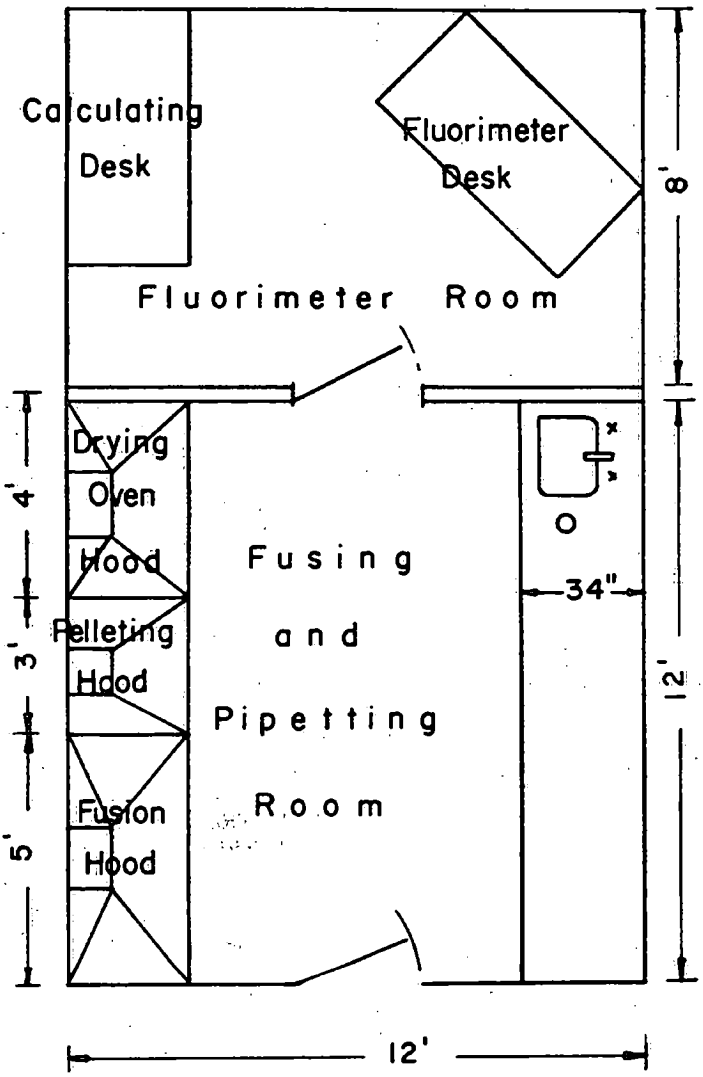


FIG. 3—FLUORIMETER ASSAY LABORATORY

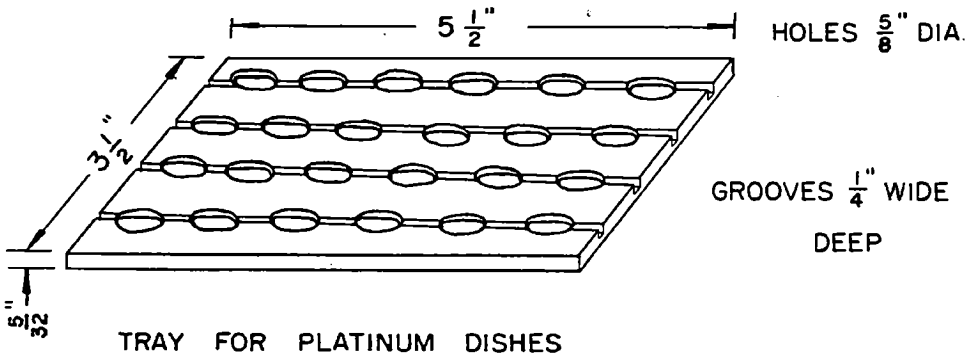
in the upper portion to protect the exhaust fan) is required (*see* Figure 14). This hood should have a face velocity of 150-200 linear feet per minute with a 1-foot sash opening. In operation, the sash is removed and a sliding panel of ¼-inch asbestos board with an 8-inch × 8-inch mica window to shield the operator while providing for observation of the flame, is used. A second small hood is required for pelleting sodium fluoride to prevent ingestion of this very poisonous substance by the operator. This hood can be omitted if pre-formed pellets are used.

APPARATUS

a) General

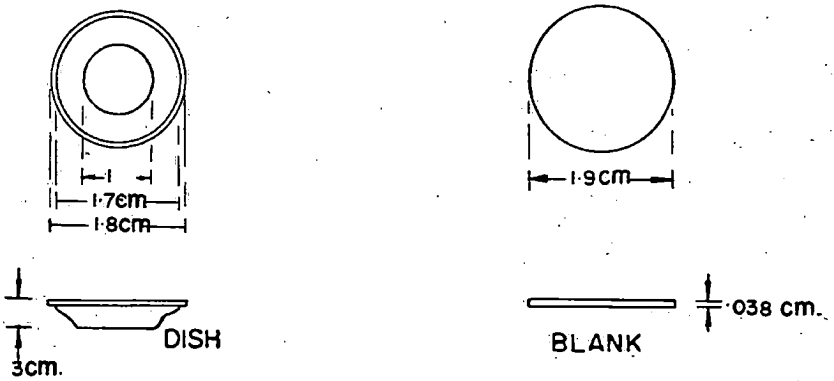
Analytical balance:	
Meker gas burners:	
Beakers:	100-ml Griffin, low form, Pyrex; *250-ml Griffin, low form, Pyrex; 600-ml Griffin, low form, Pyrex.
Crucibles, porcelain wide form:	Coors No. 1A.
Crucibles, nickel:	50-ml. capacity.
Erlenmeyer flasks:	Pyrex, 250-ml.
Separatory funnels:	Pyrex, Squibb pear shaped 60-ml 125-ml.
Separatory funnel racks:	
Bottle:	Pyrex 12 l capacity.
Valve quick-fill ½-inch brass:	Crane No. 432.
Burettes, automatic acid dispensing:	100-ml capacity screw cap type to fit regular acid winchesters. (These can also be used to dispense ethyl acetate if an aluminum adapter is used in place of the plastic one supplied).
Funnels:	Bunsen filtering long stem Pyrex glass, fluted, 75-mm diam.
Support, funnel:	Adjustable 6-hole or 12-hole hardwood rack.
Pipette, Mohr type, graduated:	10-ml capacity.
Pipette washer, siphon type:	Similar to Fisher 15-349-10.
Rubber pipetting bulbs:	15-ml capacity.
Pipettes, volumetric: (for sample dilution)	0.5, 1.0, 2.0, 5.0 and 10.0-ml.
Volumetric flasks:	50, 100, 250, 500, 1000 and 2000-ml.
Bottles, wide mouth, glass stoppered:	30-ml size.
Pipettes (for final aliquot):	0.3-ml Mohr type, 0.05-ml divisions (custom-made).
or	0.2-ml Mohr type, 0.05-ml divisions (standard).
Micropipettes, self-adjusting:	50 and 100 λ Similar to Microchemical Specialties Co. Cat. No. 283 a.
Platinum dishes:	Pressed from ¾-inch x 0.015-inch dead-soft platinum discs (*see* Figure 5 for detail).

* These are weakened by the hydrofluoric acid used in dissolving samples by the multi-acid method and have a relatively short life. They are tested by tapping them sharply before weighing samples into them.



TRAY FOR PLATINUM DISHES

FIGURE 4



DETAILS OF PLATINUM DISH FOR FLUORIDE BEAD

FIGURE 5

Dish forming tool:	Custom-made or Jarrell-Ash 2610.
Trays for platinum dishes:	(Figure 4) Trays should be given consecutive numbers and one end should be distinctively marked or the individual rows numbered.
Platinum-tipped forceps:	6-inch length.
Powerstat 2 KVA (16.7 amps):	Superior Electric Co.
Stopwatch and holder:	
Peroxide bomb apparatus:	(*See* Figures 22 and 23) Parr Electric ignition bomb, Series 2200, 42-ml cup. The assembly consists of one complete bomb with electric ignition head, fusion cup, bell body and screw cap coupling nut.
Extra fusion cups:	Parr 115 AC.
Dust covers:	Parr 146 AC.
Wrench and bench socket:	
Water bath:	Parr A 140 AC.
Peroxide dipper:	Parr A 34 C4.
Extra gaskets:	Parr 120 AC.
Ignition unit:	Parr 2901.
Crucible tongs:	
Heavy metal block for cooling dried bomb:	
Safety glasses or goggles with glass eyepiece (not celluloid or other organic type):	
Apparatus for storing salting solution—	
Reaction kettle, 3-neck:	Similar to Ace 6476, 6486 (all 3 joints 24/40).
Condenser, water-cooled:	with 24/40 joint.

Apparatus for storing salting solution—*con.*	
Thermometer well:	Ace 5295 J, 24/40.
Thermometer:	0-150° C.
Glass stopper:	24/40.
Heating mantle, electric:	similar to Ace 6478.
Variac:	0-135 volts, 7.5 amperes.
Stoppers, rubber No. 0:	boiled twice in ethyl acetate for 10 minutes.
or	
Stoppers, polyethylene No. 1:	for separatory funnels.

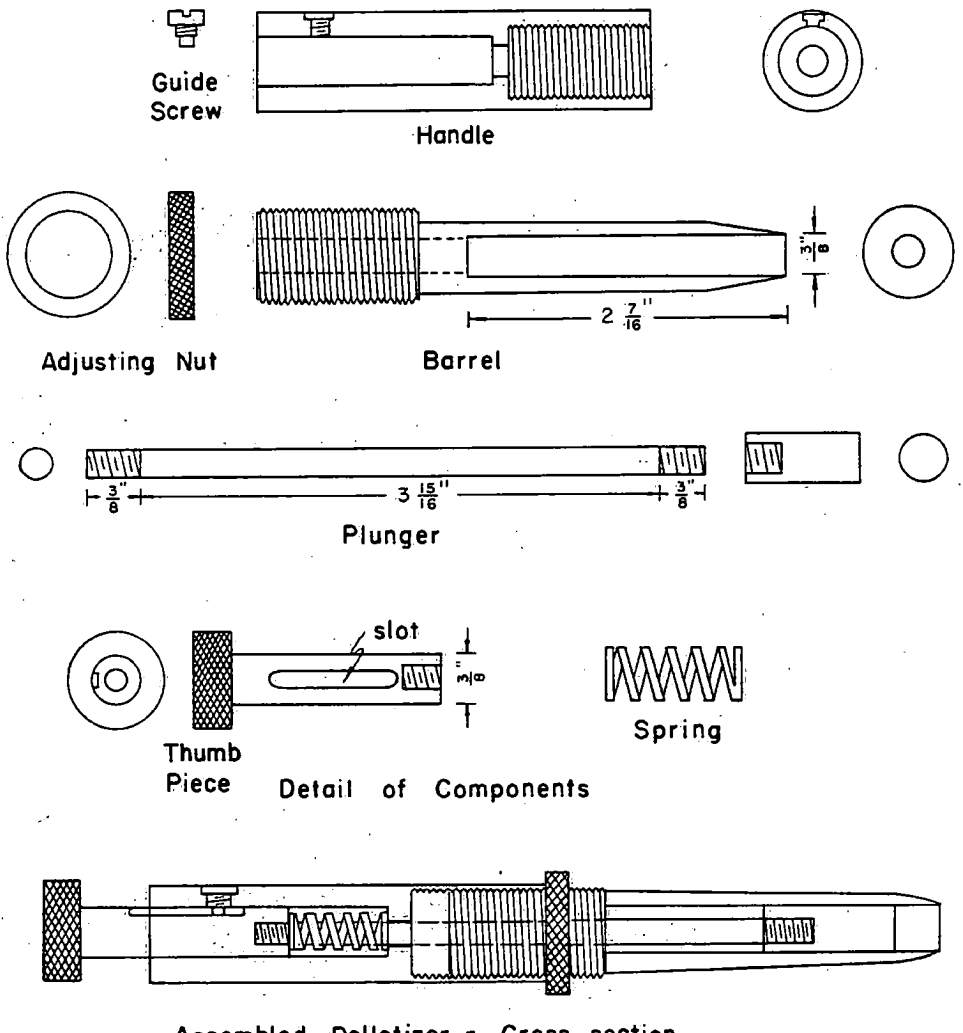


FIG. 6—SODIUM FLUORIDE PELLETIZER

Infra-red dryer:	An enclosed transite box containing four 100-watt GE Industrial type infra-red lamps, controlled by a 2 KVA Powerstat.
Pelletizer:	For producing sodium fluoride pellets. *See* Figure 6 for construction details. The pelletizer is adjusted to produce pellets 0.7-0.8 grams in weight. The pellets must be uniformly ± 0.025 grams the chosen weight.
	Sodium fluoride-lithium fluoride (98:2) pre-formed tablets have been made available commercially, under the aegis of this Division, and their use is recommended.

b) The Gas Burner and Its Adjustment

Gas burner

For fusing beads from pellets, a Fletcher radial flame burner, modified as in Figures 8 and 9 is used. A loose roll of bronze screen wire (16-mesh) about 6 inches long is inserted in the burner barrel to diffuse the gas. The end of the roll projecting into the burner bowl is reinforced with additional screening for about one inch, to provide a tighter roll. This roll of wire is moved along the barrel until a position is reached such that the gas flame is even over the whole burner top. The Nichrome V wire screen supported by short straight lengths of Nichrome V wire fastened to an 8-inch cast iron tripod ring, is mounted $\frac{1}{2}$ to $\frac{3}{4}$ inch above the surface of the burner cap and serves to hold the dishes over the flame.

Gas burner caps

Extra caps for the Fletcher burner should be kept on hand since they become warped with use and must be replaced. The new cap must be fitted as tightly as possible using a hammer to prevent gas leaking around it and burning at the edge which accelerates warping. Heavy nickel plating prolongs the life of the caps.

Nichrome wire screens

Circles of 5-mesh, 16-gauge Nichrome V wire screen, $4\frac{1}{2}$ inches in diameter should also be kept on hand. It is this screen which supports the platinum dishes.

Flame adjustment (Vacuum cleaner air supply)

Turn on the gas and ignite it. Adjust the gas and air controls to give a flame in which the bright blue unburnt gas cones are $\frac{1}{4}$ to $\frac{3}{8}$ inch high and of even height over the whole burner. (If the flame is not even, shut off the burner, take it apart and adjust the screen wire baffle.) Then increase the air flow, using the air escape port and the set-screw, Figure 10, until the burner "howls". Cut the air back just sufficiently to prevent the howling, and leave the air setting in this position. Note the reading on the gas gauge, mark for reference, and then shut off the burner.

Measure 0.7 gram of sodium fluoride into each of 22 dishes, using the same technique as in preparing samples. Place them on the Nichrome screen support over the burner. Turn on the gas and ignite it. Leaving the air control as previously set, quickly adjust the gas to approximately the same gauge reading as before, and start the stop watch. By means of further small adjustments of

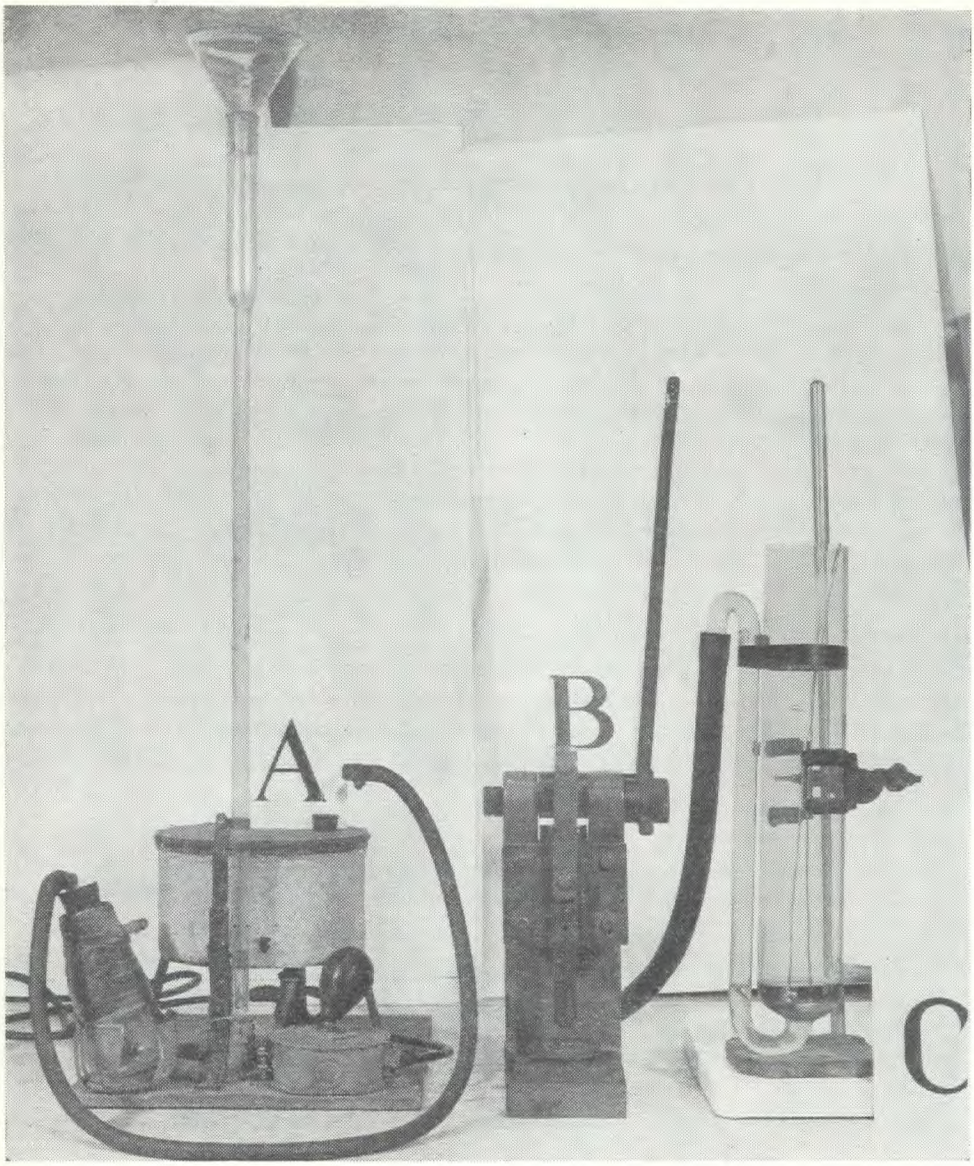
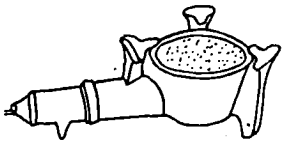


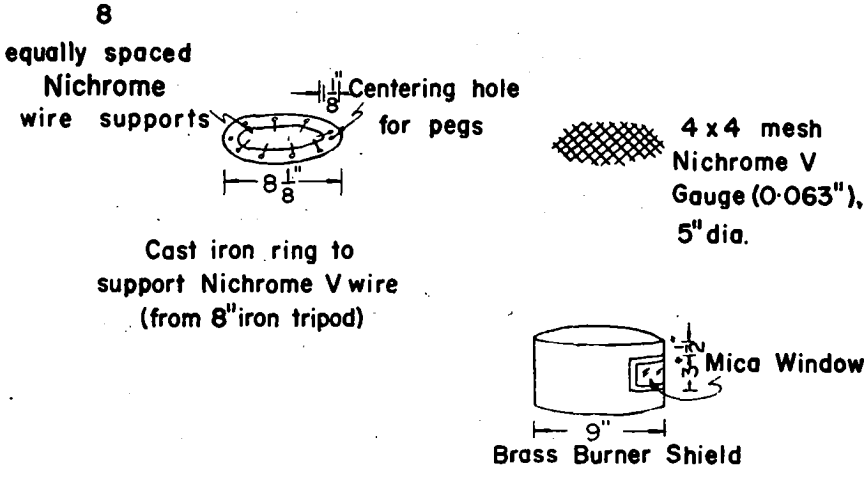
FIG. 7—A. STEAM GENERATOR. B. DISH PRESS. C. PIPETTE WASHER

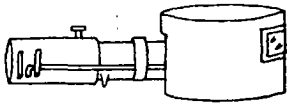
the gas control adjust the flame so it just stops "howling". Note the time it takes for the pellets to melt. If they take longer than $1\frac{1}{2}$ minutes, repeat the burner adjustment using a larger gas flow. If they melt too quickly adjust the burner using a smaller gas flow. Once the proper adjustment is obtained, leave the air control as set and control the flame which is just hot enough to melt the pellet in the $1\frac{1}{2}$-minute period. Melting too rapidly leads to quenching. On the other hand, too slow a fusion wastes gas and may result in quenching.



BURNER: Fletcher Radial

Flame as received from supplier





Assembled Burner

(Compressed Air Supply)

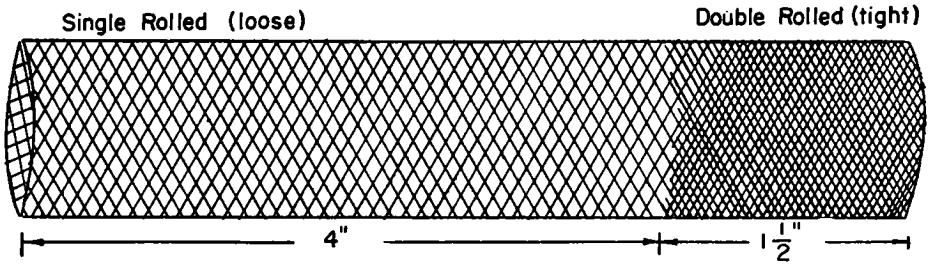
FIG. 8—DETAILS OF MODIFIED FLETCHER RADIAL FLAME BURNER (I)

Flame adjustment (compressed air supply)

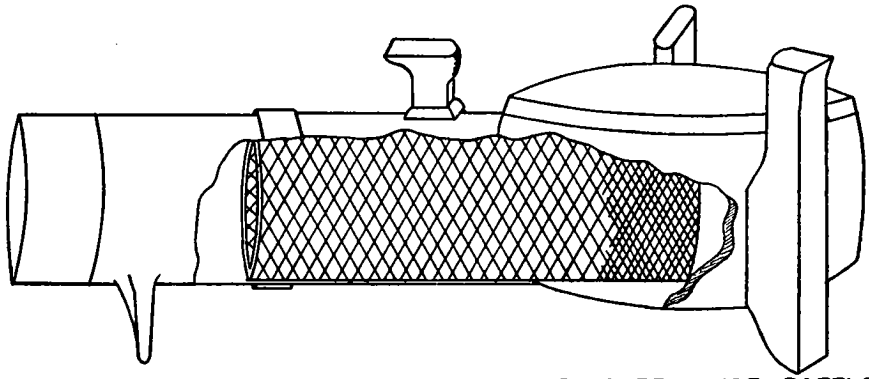
The method employed is exactly the same as for the vacuum cleaner air supply except that it may be necessary to use a fixed gas flow as indicated by the gauge and control the flame by means of the air adjustment, (when the proper gas setting has been established.)

c) Air Supply

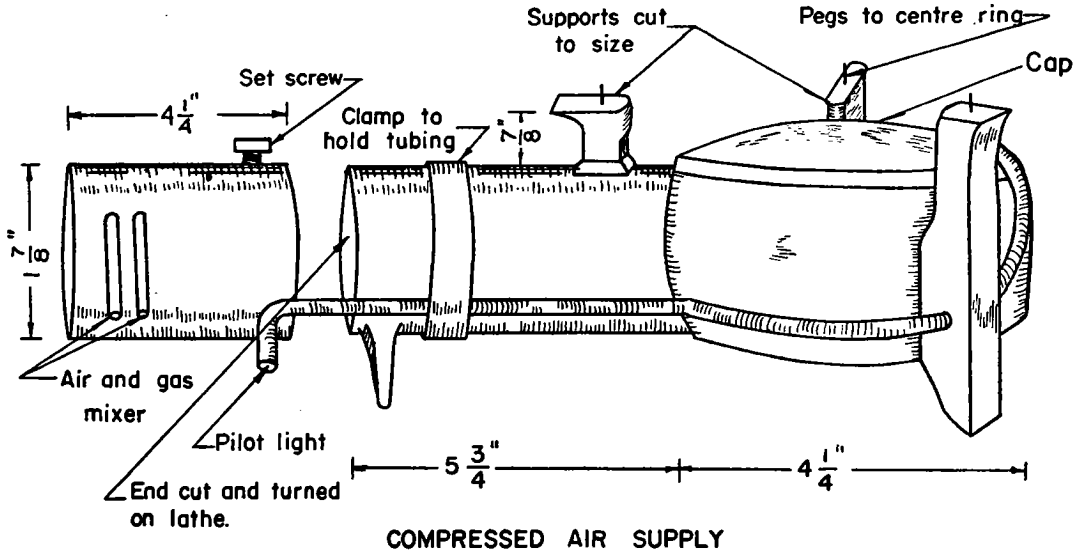
The burner may be modified to use either compressed air from the laboratory supply, or air from a household vacuum cleaner. In the latter case, the vacuum cleaner serves as an individual air supply which is to be preferred,



SCREEN WIRE BAFFLE



CUTAWAY VIEW OF BURNER SHOWING POSITION OF SCREEN WIRE BAFFLE



COMPRESSED AIR SUPPLY

FIG. 9—DETAILS OF MODIFIED FLETCHER RADIAL FLAME BURNER (2)

since sudden demands on the regular compressed air supply elsewhere may render it unreliable. The air-supply modification is shown in Figure 8. Figures 10 and 11 show the adapters for converting to vacuum cleaner air supply.

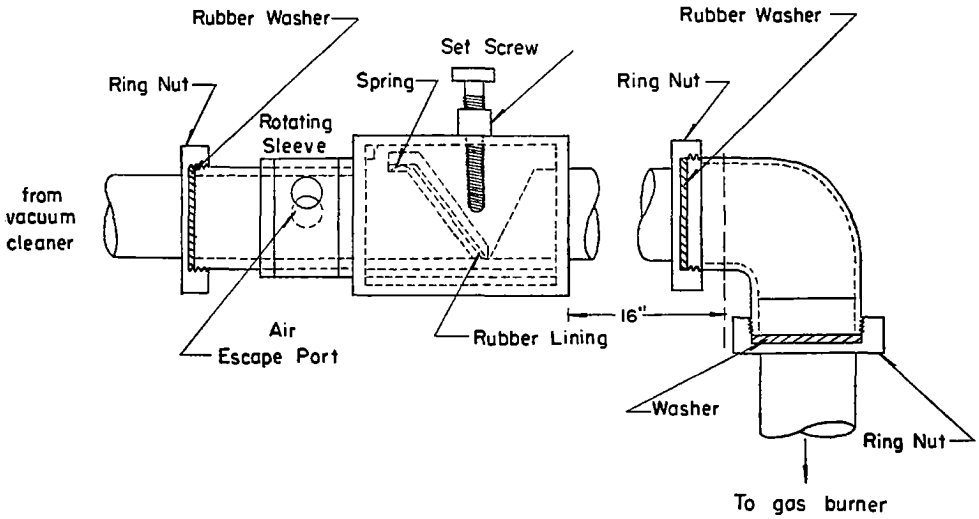


FIG. 10—VACUUM CLEANER AIR CONTROL

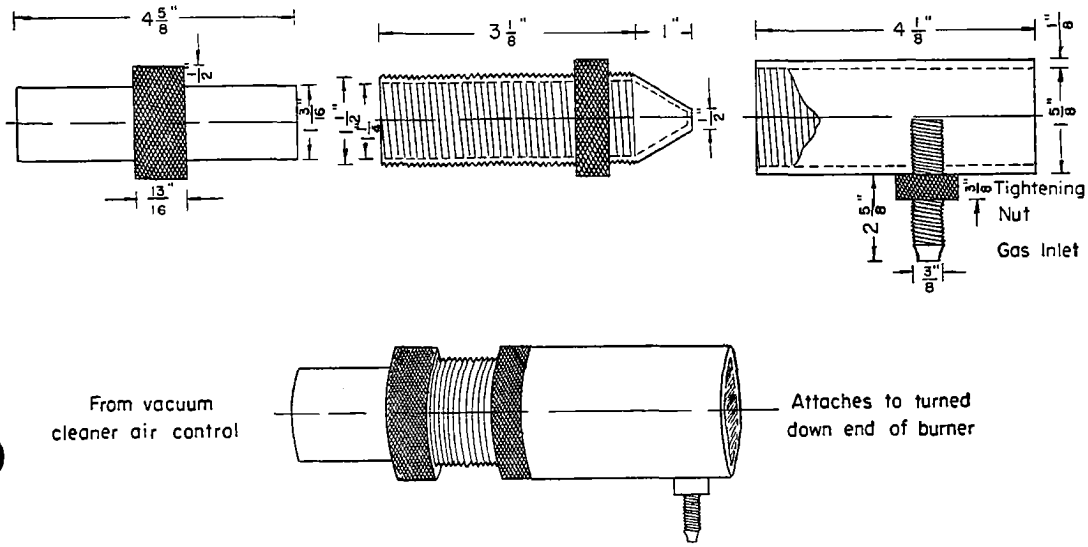


FIG. 11—AIR AND GAS MIXER USED WITH VACUUM CLEANER AIR SUPPLY

d) Gas Supply

Propane gas supplied by one of the commercial two-cylinder services is used.

About one 100-lb. cylinder per 1000 samples is required in Ottawa. At Port Radium, gas is used at about twice this rate. In northern areas, these cylinders must be enclosed in a heated enclosure or three cylinders must be used in parallel, to obtain the desired gas flow. (Insurance regulations do not permit keeping the cylinders in the laboratory proper.) Table 1 (9) gives the vaporization rate in cubic feet per hour for the cylinders at various temperature and cylinder contents. It is apparent that in cold situations the cylinders cannot be utilized completely. Utilization per cylinder can be increased by using more cylinders in parallel.

Table 1

Vaporization Rate of Propane in 100-lb. Cylinder in Cubic Feet per Hour

Contents of Cylinder, lbs. propane	Temperature °F							
	0°	10°	20°	30°	40°	50°	60°	70°
100	45.5	55.7	67.0	77.3	85.8	94.5	111.0	120.0
90	42.2	51.5	60.9	70.0	80.0	85.8	103.0	111.0
80	37.8	46.4	54.9	63.5	72.0	80.6	85.8	94.5
70	33.5	41.3	48.9	56.6	64.0	72.0	79.6	85.8
60	30.2	36.9	43.6	50.0	56.0	63.5	70.4	77.0
50	25.8	31.8	37.8	43.6	50.0	55.8	61.7	67.0
40	22.3	26.8	31.7	36.9	42.0	47.4	52.4	56.6
30	18.0	22.3	26.6	30.9	34.0	38.6	43.0	47.2
20	14.6	17.3	20.6	24.0	27.5	30.0	33.4	36.9
10	11.3	12.9	15.4	17.3	19.7	22.3	24.0	26.6

Gas gauge

This gauge (Figure 12) actually indicates the gas pressure in the line from the cylinder to the burner. The drop in pressure when the burner is in operation serves to indicate the rate at which gas is being used and can be used as a guide in obtaining the proper flow. It cannot be permanently calibrated since the initial line pressure varies.

e) Steam Supply

After fusion the gas is cut off and the beads are cooled in a steam atmosphere. Process steam, suitably filtered and trapped may be used or an electric steam generator similar to that shown in Figure 7 may be constructed or improvised from an electric kettle. The purpose of cooling in a steam atmosphere is to prevent solution of platinum by fluoride which occurs under oxidizing conditions. During the fusion, the burnt gas atmosphere protects the dishes and therefore the critical period is after the gas is shut off, before the beads have cooled. Platinum acts as a quencher and beads so quenched have a pink or brown appearance. Good beads are brilliantly white.

f) MIT Model 3 Fluorimeter

This is a custom model used at the Mines Branch and constructed at the Massachusetts Institute of Technology Mineral Dressing Laboratory, Boston, Mass. It is shown in Figure 13 and schematically in Figure 15.

The circuit diagram for the regulated high voltage supply to the 1 P 21 photomultiplier tube is shown in Figure 16. It is supplied with 110 volts AC stabilized by a GE 69 G 851 100-watt stabilizing transformer. The 300-volt

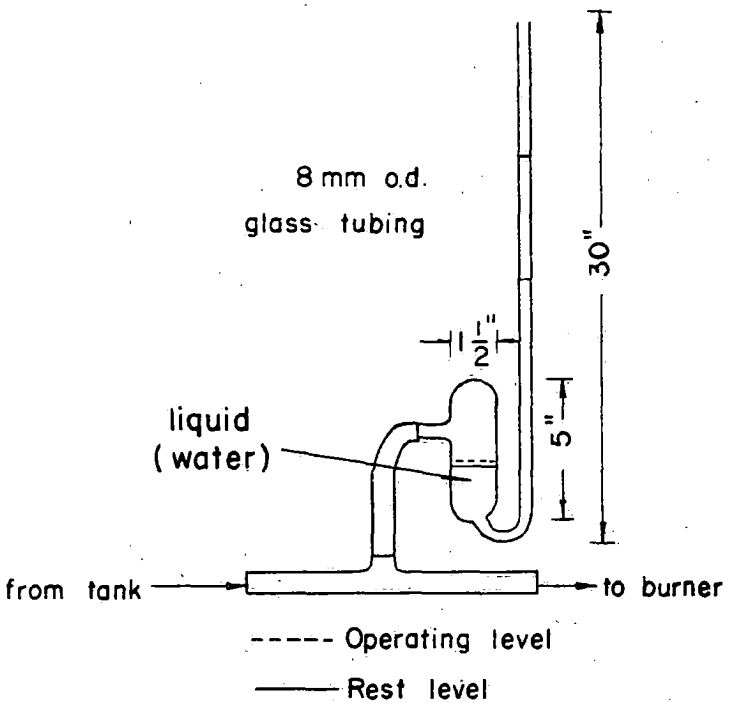


FIG. 12—GAS CONTROL GAUGE

battery of this power supply should be replaced every year. The four 100-watt, General Electric A H 4 mercury vapour lamps used to irradiate the beads with ultra violet light are supplied by individual General Electric No. 89 G 142 Auto Transformers. Light to the beads is filtered through Corning No. 5860 black glass filters (0.5 cm thickness, approx 13% transmission) to provide monochromatic light of 365 mμ wave length. The fluorescent light from the beads is filtered free of stray light and reflected ultra violet light by a Corning No. 3484 traffic light yellow filter. The filtered fluorescent light, after passing through a condensing lens is again filtered through a Corning No. 9780 blue green filter which passes the 550 mμ wave length of uranium fluorescence (10) but filters out the fluorescence excited in the yellow No. 3484 filter by the stray ultra violet light it stops.

The output of the 1 P 21 tube is measured with a triple reflection fibre suspension Rubicon No. 3414 galvanometer, sensitivity 0.0015 μ a per mm. with a full scale deflection of 10 cm. The galvanometer is shunted by a Rubicon Ayrton shunt of 10,000 ohms total resistance having a manual switch which permits multiplying factors of 1, 10, 100, 1000 and 10,000. The principle of the Ayrton shunt (13) depends on matching the total resistance of the shunt to the internal resistance of the galvanometer (information supplied on a tag on the galvanometer base). This should be kept in mind if for any reason either must be replaced.

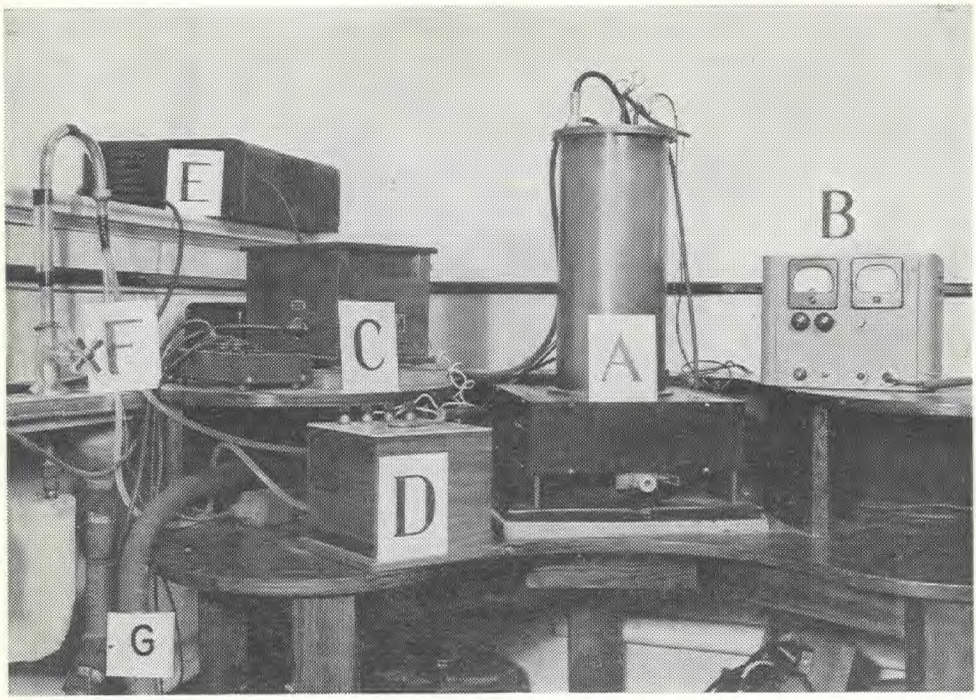


FIG. 13.—THE MIT MODEL 3 FLUORIMETER

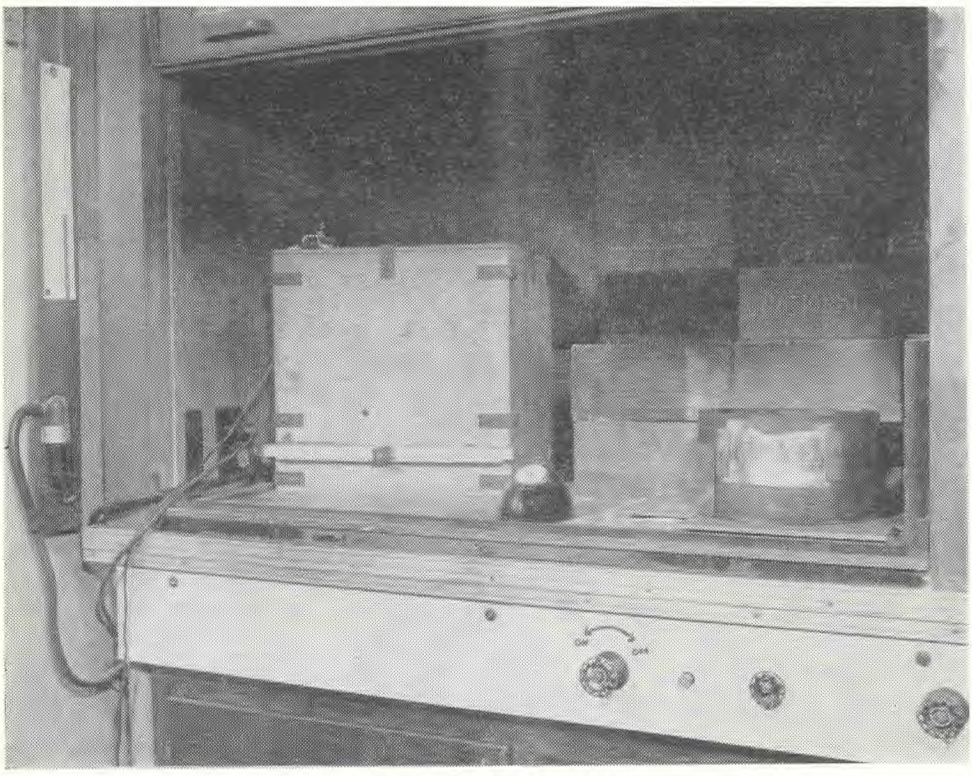


FIG. 14.—THE FUSION HOOD

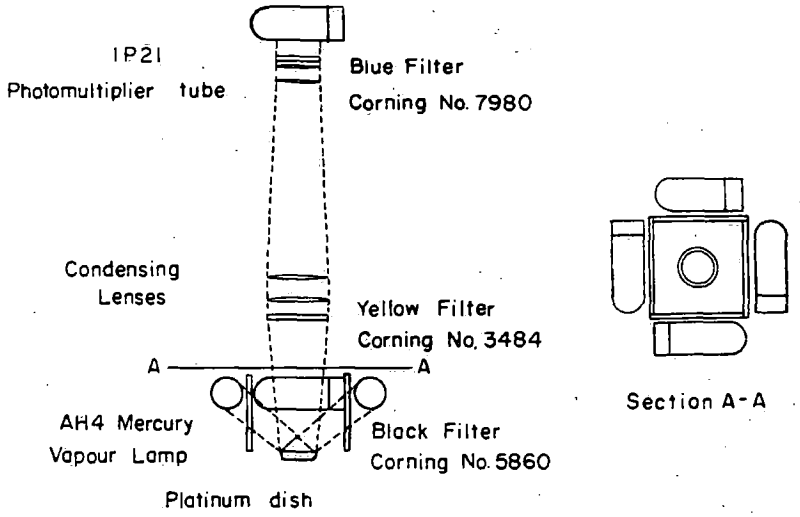


FIG. 15—SCHEMATIC DIAGRAM OF MIT MODEL 3 FLUORIMETER

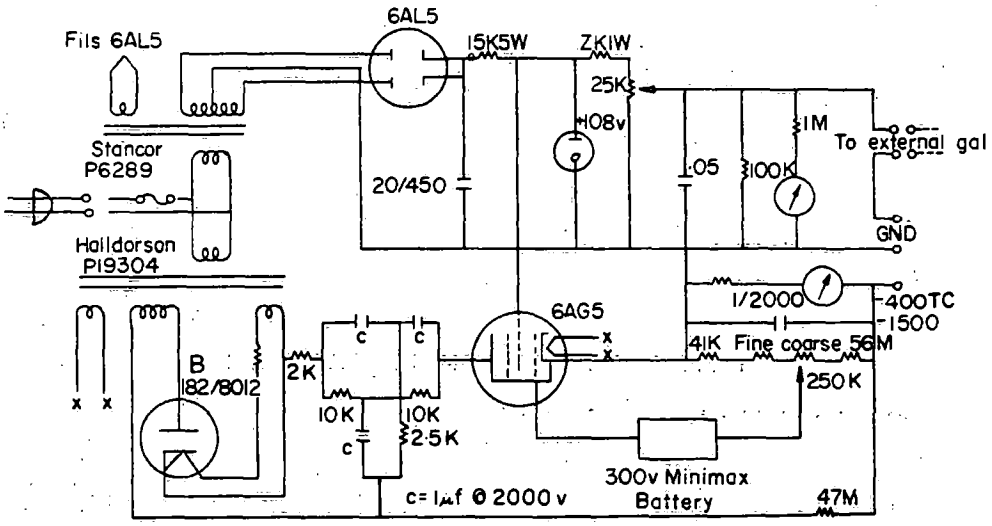


FIG. 16—HIGH VOLTAGE SUPPLY, MIT MODEL 3 FLUORIMETER

Spares and Replacements for the M.I.T. Fluorimeter

Mercury vapour lamps—Four 100-watt G.E. AH 4 lamps. *These lamps must never be started up while still hot.* If the power goes off, shut the instrument off at once. Once off, always allow a 10-minute wait before turning on again.

Spare filters—4 pieces, $\frac{3}{4}''$ x $1\frac{1}{4}''$, Corning 5860, 0.5 cm thick.

The filters can break if the cooling system is not turned on. Also during periods of high humidity, atmospheric condensation inside the instrument dropping on the hot glass may crack it.

Colloidal graphite (aqueous or alcoholic solution)—used to touch up any reflecting surfaces in the path of the light detecting system.

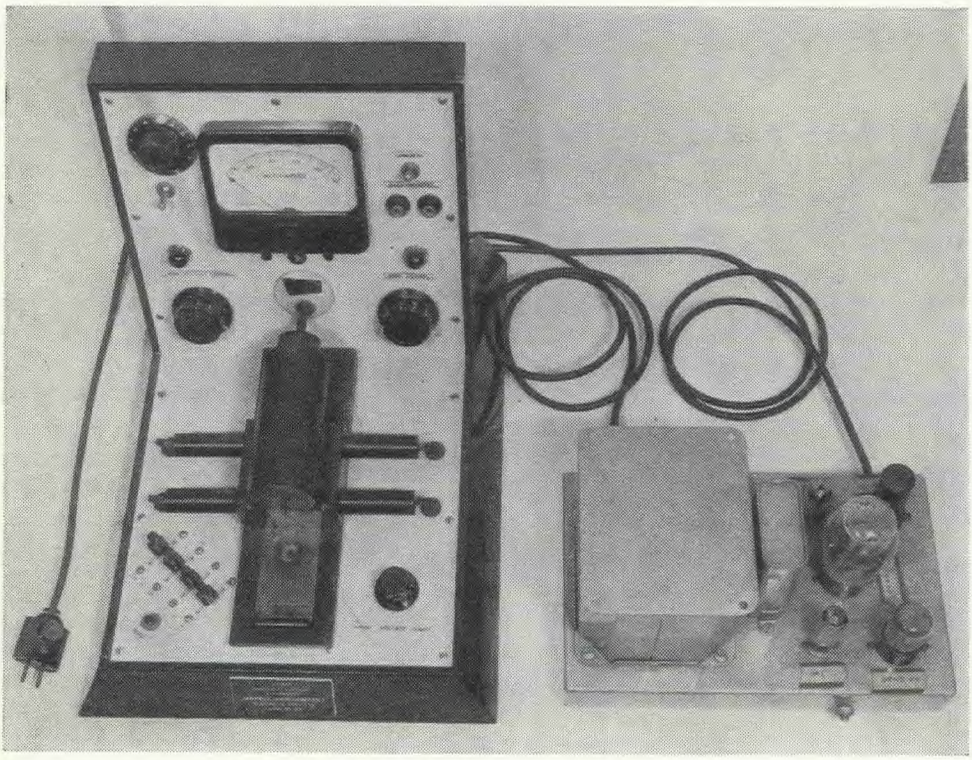


FIG. 17.—JARRELL-ASH GALVANEK-MORRISON FLUORIMETER

g) Galvanek-Morrison Fluorimeter

This is the best known commercially available fluorimeter and therefore the one most likely to be used in the mill control laboratory. The one used at the Mines Branch, together with its power supply, is illustrated in Figure 17. The circuit diagram is shown in Figure 18A.

The ultra violet source consists of two 4-watt fluorescent-type ultra violet lamps in close proximity to the bead. These lamps do not require cooling.

The detecting unit is mounted above and between the two ultra violet lamps and scans the bead directly, through a filter system similar to that used in the M.I.T. Model 3 instrument. It consists of an RCA 1P 21 photomultiplier tube. A mu-bridge type vacuum tube regulated power supply provides up to

700 volts DC for the operation of the photomultiplier tube. Coarse and fine voltage controls are provided to regulate the voltage supplied to the photomultiplier tube. This enables the photomultiplier output, which is the indication of the fluorescence of the bead and therefore its uranium content, and which is indicated by the microammeter on the face of the instrument, to be adjusted to some convenient value when the standard is in place. (*See* also note on Power Supply). A background compensating control is provided to balance out the phototube dark current.

A two-position slide is provided for the phosphor beads. The innermost position contains a suitable permanent standard so that it is in position when the slide is out to permit inserting the sample and at the same time the meter is connected automatically to the 0.01 range, providing a convenient means for checking the standard setting.

The measuring system of the instrument consists of a vacuum tube voltmeter of the symmetrical differential type. A series of range switches in keyboard arrangement corresponds to the shunt of the M.I.T. instrument. When the sample is introduced into the light chamber, the meter is automatically set to its highest range, providing protection for the microammeter. The sample reading is then the microammeter reading multiplied by the scale factor for the range switch used to obtain the maximum reading of the microammeter.

The stability of the instrument can be improved by a change in the vacuum-tube voltmeter circuit (*See* Figure 18B). Instead of directly grounding the control grid connected to pin 1 of the 6 SN 7 W tube, a new resistor, R 44 (5.6 megohms, ½ watt) is inserted between the pin and ground. This resistance, which is equal to the resistance (R10) between the other control grid and ground, balances any biassing due to grid current resulting from gas in the tube.

Power Supply—The power supply is adjusted to provide 700 volts total. (The voltage applied to the photomultiplier tube is about 600 volts total.) This adjustment can be changed or corrected when tubes are changed, by turning the screw shown on the front of the power supply (Figure 17). Occasionally it will be found that the Coarse and Fine Voltage Controls will not permit setting the microammeter to the desired reading with the standard bead, the value at one coarse setting being too low and at the next too high. In this case, set the Coarse Voltage Control at the setting just before the one in which it gives too high a reading, set the Fine Voltage Control in the middle of its range and adjust the setting of the screw on the power supply till the desired reading is obtained.

The following circuit change is recommended to improve tube life. As presently connected (*see* original wiring diagram, Figure 18A) there is a potential of 150 volts between the heater winding and the cathodes of the 6 SL 7 GT tube. The *maximum* potential difference recommended by the tube manufacturer is 90 volts. Connecting the new resistors R 42 (470 K ohms, ½ watt) and R 43 (120 K ohms, ½ watt) in series, placing them in parallel with the present R 39 (25 K ohms 25 watt), and tying the heater-winding to the junction of R 42 and R 43, reduces this potential to not more than 70 to 80 volts.

A complete original circuit diagram is given in Figure 18A, a revised circuit is shown in Figure 18B, and a parts list is given below.

The instrument is less sensitive and precise than the M.I.T. instrument, but is very convenient to use. Absence of a lens system makes it subject to

some variability in reading depending on the orientation of the bead in the holder, and it is suggested that two or more readings of each bead be averaged, rotating the bead 60° in the holder between readings. Occasionally it may be necessary to adjust the position of the photomultiplier tube in its mount so that

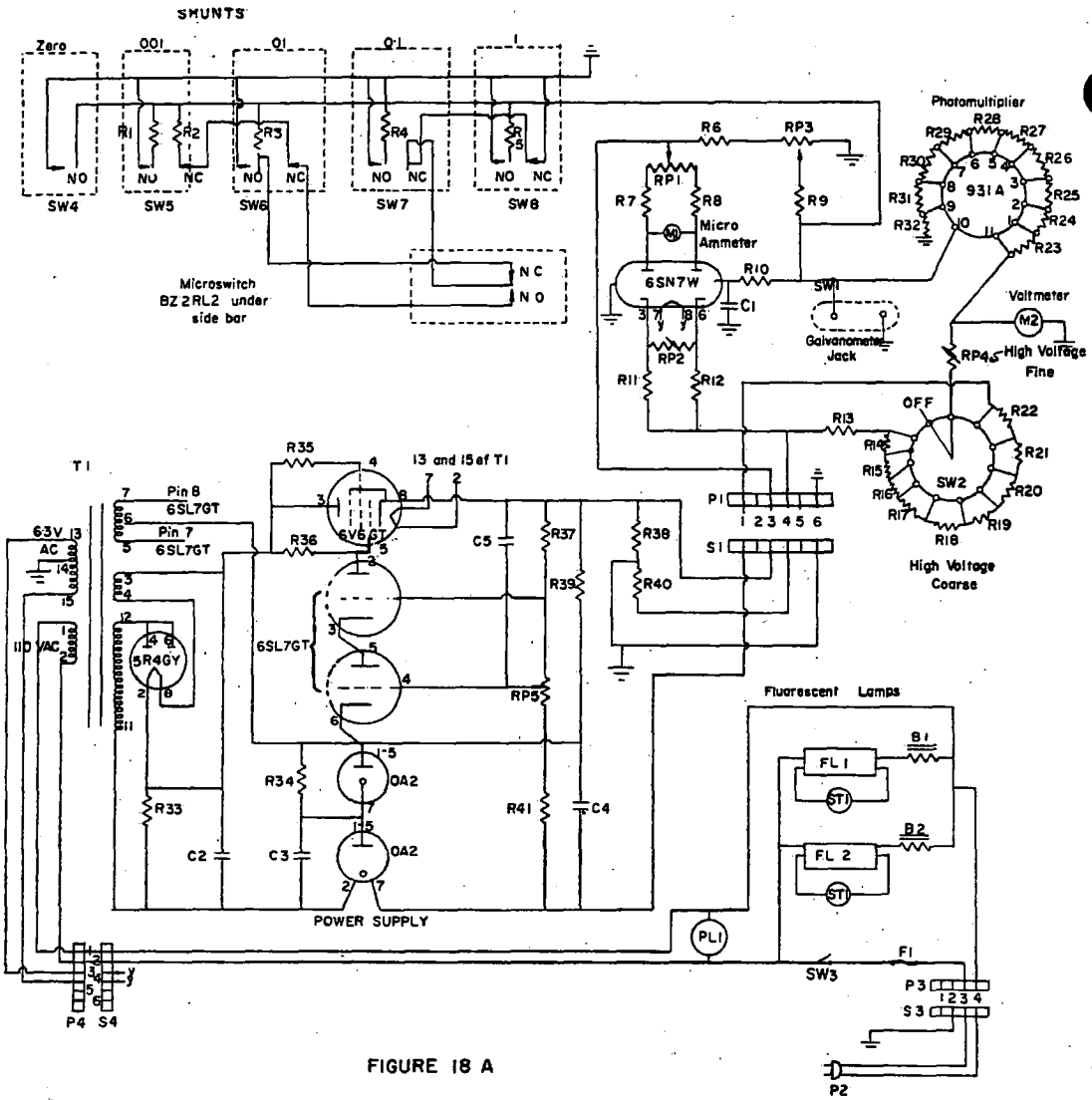


FIGURE 18 A

WIRING DIAGRAM JARRELL-ASH GALVANEK-MORRISON FLUORIMETER

the fluorescence from the beads falls again on the most sensitive portion of the cathode of the photomultiplier tube. In the Mines Branch instrument, voltage fluctuations change the zero reading, so use of a voltage stabilizer ahead of the instrument is recommended.

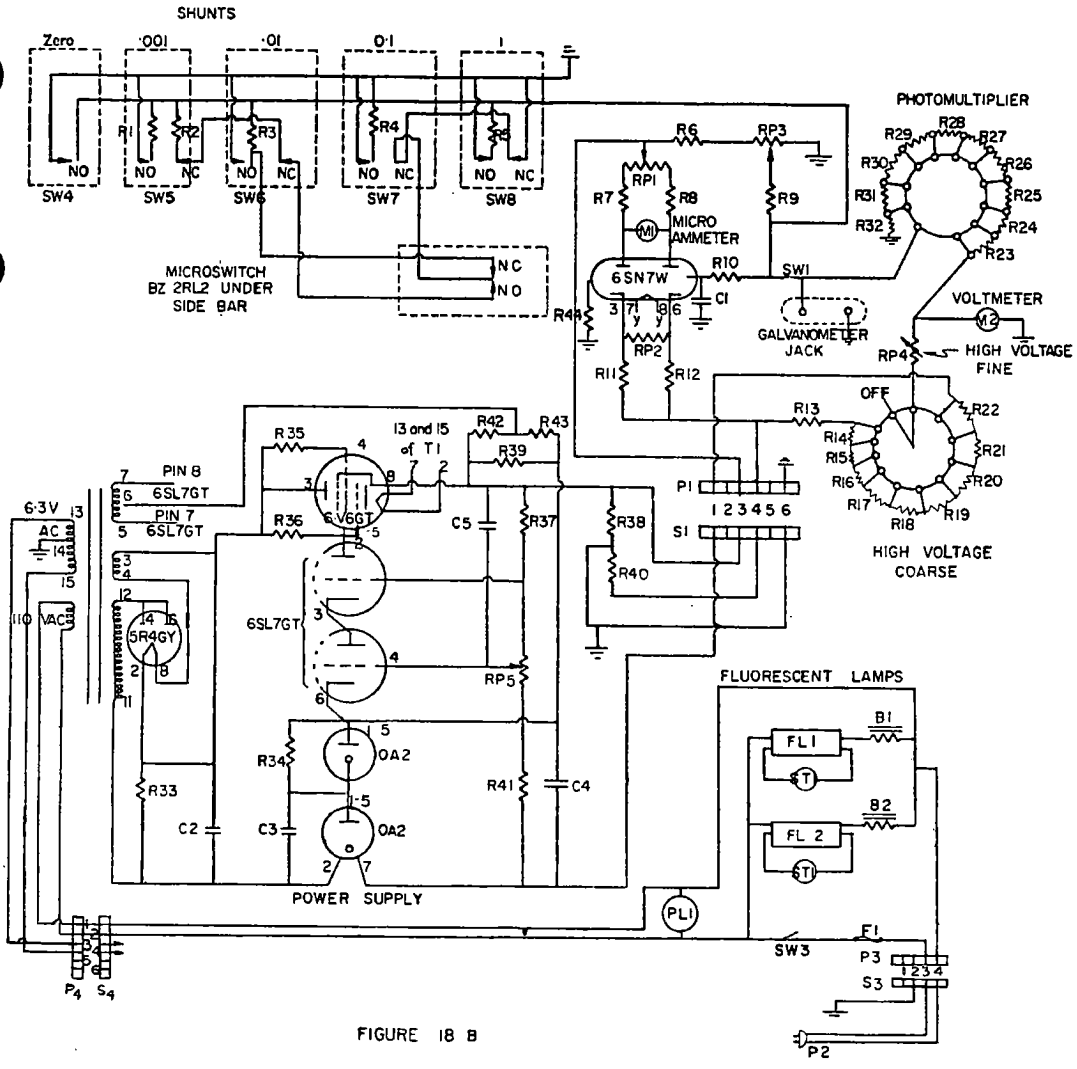


FIGURE 18 B

REVISED WIRING DIAGRAM JARRELL-ASH GALVANEK-MORRISON FLUORIMETER

Parts List for the Galvanek-Morrison Fluorimeter (See Figure 18A)

*Triode tube 6 SN7W
*Rectifier tube 5 R4GY
*Control tube 6 V6GT
*Control tube 6 SL7GT
*Regulator tube OA 2
*Photomultiplier tube 932 (1P21)

* Items that should be stocked as spare parts.

Parts List for the Galvanek-Morrison Fluorimeter—Continued

*B1	Ballast GE 89 G 435—4 Watt 60 cycle	
*B2	Ballast GE 89 G 435—4 Watt 60 cycle	
C1	Condenser Cornell Dubiler No. P J4S 22 Tiny Chief .022mfd 400 volts DC	
C2	Condenser Aerovox type 09, 2mfd, 1500 VDC	
C3	Condenser Cornell Dubiler type, Cub 6S3 .03mfd 600 VDC	
C4	Condenser Cornell Dubiler type, Cub 6S5 .05mfd 600 VDC	
C5	Condenser Cornell Dubiler type, Cub 6P1 0.1 mfd 600 VDC	
*F1	Fuse 6 amp Fustron type MTH	
*FL 1	Fluorescent tube, 4 watt Sylvania F-F4T5-BL-B	
*FL 2	Fluorescent tube, 4 watt Sylvania F-F4T5-BL-B	
M1	Microammeter Simpson model 29, 0-100 DC also Triplett model 426	
M2	Voltmeter Simpson model 125, 0-750 DC	
P1	Male connector Jones P-306 AB	
P2	Male connector type HRA	
P3	Male connector Jones P-304 AB	
P4	Male connector Jones P-306 CCT	
*PL 1	Pilot light assembly Dial Co 521308-997	
R1	Resistor	2.5 meg ohms, 1 watt ± 1%
R2	Resistor	250 ohms, 1 watt ± 1%
R3	Resistor	250K ohms, 1 watt ± 1%
R4	Resistor	25K ohms, 1 watt ± 1%
R5	Resistor	2.5K ohms, 1 watt ± 1%
R6	Resistor	100K ohms, 2 watt ± 10%
R7	Resistor	820 ohms, 2 watt ± 10%
R8	Resistor	820 ohms, 2 watt ± 10%
R9	Resistor	20 meg ohms, 2 watt ± 10%
R10	Resistor	5.6 meg ohms, 2 watt ± 10%
R11	Resistor	22K ohms, 2 watt ± 10%
R12	Resistor	22K ohms, 2 watt ± 10%
R13	Resistor	22K ohms, 2 watt ± 5%
R14	Resistor	15K ohms, 2 watt ± 5%
R15	Resistor	10K ohms, 2 watt ± 5%
R16	Resistor	6.8K ohms, 2 watt ± 5%
R17	Resistor	5.6K ohms, 2 watt ± 5%
R18	Resistor	4.7K ohms, 2 watt ± 10%
R19	Resistor	3.9K ohms, 2 watt ± 10%
R20	Resistor	2.2K ohms, 2 watt ± 10%
R21	Resistor	1.5K ohms, 2 watt ± 10%
R22	Resistor	1K ohms, 2 watt ± 10%
R23 to 32	Resistor	100K ohms, ½ watt ± 10%
R33	Resistor	1 meg ohm 2 watt ± 10%
R34	Resistor	1 meg ohm 2 watt ± 10%
R35	Resistor	150 ohms, 2 watt ± 10%
R36	Resistor	5.6 meg ohms, 2 watt ± 10%
R37	Resistor	120K ohms, 2 watt ± 10%
R38	Resistor	8.2K ohms, 2 watt ± 5%
R39	Resistor	25K ohms, 25 watt (Ohmite—0219)
R40	Resistor	3.9K ohms, 2 watt ± 5%
R41	Resistor	120K ohms, 2 watt ± 10%
RP-1	Resistor	Helipot 3 turn 2000 ohms

*Items that should be stocked as spare parts.

Parts List for the Galvanek Morrison Fluorimeter—Concluded

RP-2	Potentiometer Ohmite 500 ohms, Type AB 2 watt	
RP-3	Potentiometer Clarostat 20,000 ohms, Series 58	
RP-4	Potentiometer Clarostat 100K ohms, Series 10	
RP-5	Potentiometer Ohmite 100K ohms, Series 10	
SW-1	Toggle switch SPST	
SW-2	Rotary selector Mallory 172	
SW-3	Toggle switch SPST	
SW-4 to 8	Lever action switch	Central AB-1456
S1	Female connector	Jones S-306 CCT
S3	Female connector	Jones S-304 CCT
S4	Female connector	Jones S-306-AB
*ST-1	Starter	GE-FS-5 (6 watt)
*ST-2	Starter	GE-FS-5 (6 watt)
*ST-1	Transformer	United Transformer Co S-40

The following additional parts are required for the conversion suggested in Figure 18B.

R42	Resistor	470K ohms
R43	Resistor	120K ohms
R44	Resistor	5.6 meg ohms 2 watt ± 10%

h) Checking the Linearity of Instrument Response

With a new instrument it is good practice to verify that the instrument responds in a linear fashion to increasing amounts of uranium. This simply involves fusing several sets of beads using amounts of uranium covering the practical range of uranium concentrations and plotting a curve of shunt × galvanometer response against uranium concentration. A typical curve (obtained on the M.I.T. Model 3 instrument) is shown in Figure 19. In analyzing samples standards are run with each set and the curve should never be used for analysis. This is because fluorescence is a function of fusion temperature which will vary from set to set.

If the curve shows a significant departure from linearity, either the phototube or the shunt may be at fault. The individual shunt resistances should then be checked to verify that they have the specified values. The phototube can be replaced by the spare tube to see if this will improve performance.

i) Checking Fluorimeter Performance

Set aside a large amount of a well-analyzed sample. Weigh 10 portions of this sample, dissolve and carry out a single determination on each sample (4 beads), one sample with each of ten fusions. Calculate the standard deviation and absolute error.

j) Cleaning the Platinum Dishes

Remove the beads from the dishes either by gentle tapping (not hard enough to bend the dish) or by soaking in running hot water for 30 minutes. Keep all the dishes of one set together and place them in 100-ml beakers, stacking them carefully so that one dish is not fitted into another one. Cover the dishes

*Items that should be stocked as spare parts.

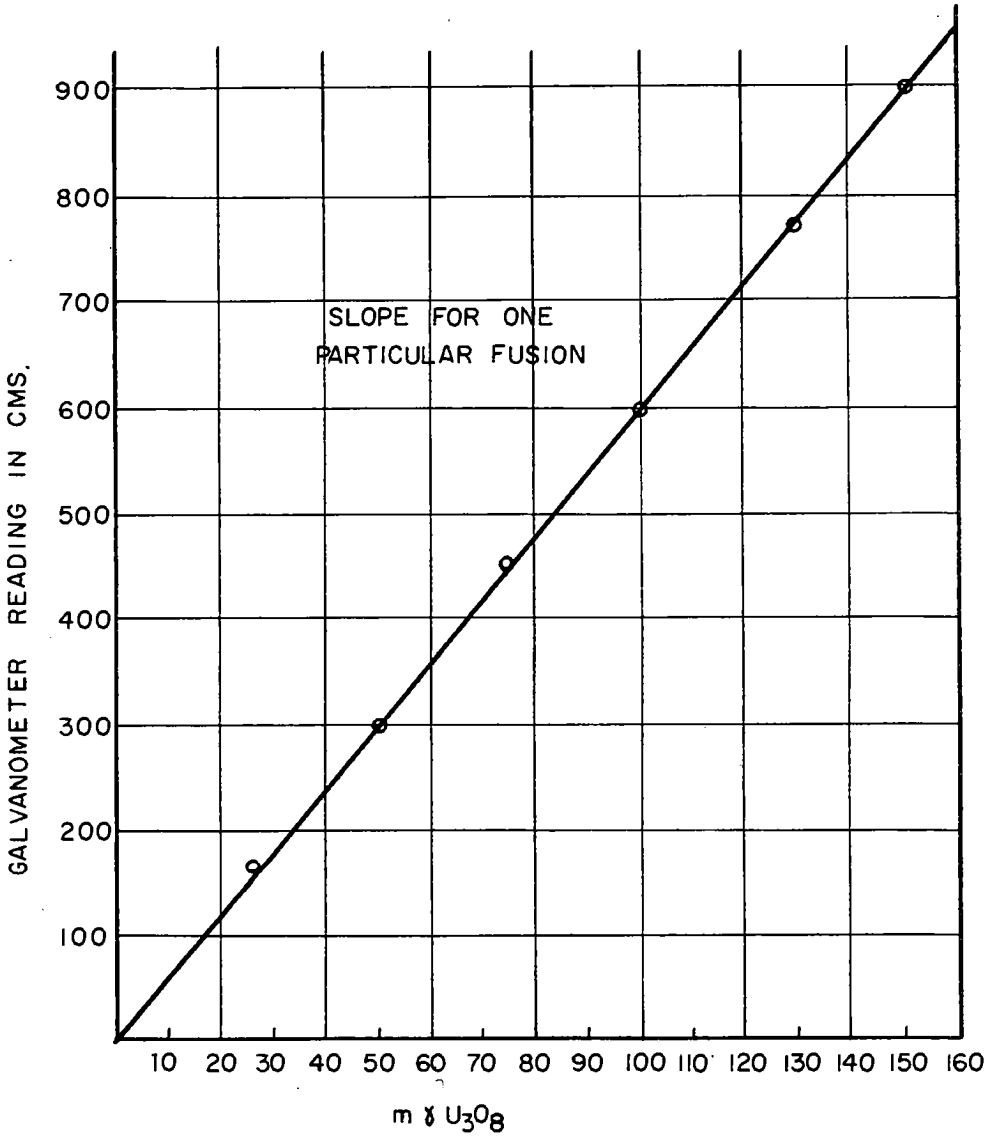


FIG. 19—CALIBRATION CURVE

with concentrated hydrochloric acid and boil them for 30 minutes. Pour off the acid and rinse well with tap water. Repeat the acid treatment and rinsing. Finally decant off the tap water, replace with distilled water and store for use. Do not touch the platinum with the fingers again until after the beads have been read on the fluorimeter.

Occasional hand buffing with a household silica detergent cleanser helps to reduce quenching from contaminants absorbed into the dishes. The dishes may also be fused in a Vycor dish with potassium bisulphate occasionally. Eventually the dishes adsorb so much iron and other quenchers that erratic results are

obtained. About once a year the used platinum dishes should be exchanged for new platinum.

Use of mixed sodium fluoride-lithium fluoride flux does not greatly reduce the necessity for cleaning the platinum dishes. The beads detach themselves readily from the platinum, but the acid cleaning treatment is still important (12). This should be supplemented by the above buffing procedure at regular intervals depending on the use, since it has been found here that after about 30 fusions, the platinum of the dish loosens up and it is no longer possible to free the bead from the dishes easily.

REAGENTS

(Quantities where given are based on 50 samples per day work load.)

Nitric acid CP:	About 50 ml per sample or 20 winchesters per month (used chiefly in diluting sample solutions).
Hydrochloric acid CP:	About 50 ml per sample or 20 winchesters per month (used chiefly in cleaning dishes).
Sulphuric acid 1:1:	Prepare in a 4-litre beaker by adding 1 litre of concentrated C.P. sulphuric acid to 1 litre of distilled water with constant stirring, cooling as required. WEAR GOGGLES. When cool, dilute to 2 litres with water.
Hydrofluoric acid:	In 1-lb. polyethylene bottles 10 ml per sample, 25 lb. per month.
Sodium peroxide:	Reagent Special (Baker and Adamson Code 2273).
Sugar charcoal:	Fisher C-272, finely ground.
Fuze wire:	Parr Cat. No. 45 C7.
Nitric acid:	1:1 v/v 5% v/v (50 ml per litre) 10% v/v (100 ml per litre)
Sodium chlorate:	Reagent grade.
Hydrogen peroxide:	30% Reagent grade.
Ethyl acetate:	Reagent grade (Merck).
Hydrochloric acid:	1:1 v/v.
Aluminum nitrate:	C.P. –A 1-lb. batch should be tested for blank and suitability before being stocked. This reagent is used at the rate of 10 determinations per lb.
Aluminum nitrate salting solution:	Place approximately 1800 grams (4 lb.) of aluminum nitrate ($Al(NO_3)_3 \cdot 9\ H_2O$) in a 4-litre beaker and add 100-200 ml of distilled water. Cover the beaker and heat the mixture on a hot plate. If a clear solution does not result after 5-10 minutes boiling, add 50 ml of water and continue boiling for 5 more minutes. Repeat this step until a clear solution is obtained after boiling. Remove the cover glass and concentrate the solution by boiling until a boiling point of 130° C is reached. This will give about 1000 ml of salting solution. Cover the beaker with a watch glass and either transfer the solution to a constant temperature apparatus or keep the solution warm, finally heating to about 110° C before use. If the reagent is to be stored, transfer to a 1000-ml three-neck reaction flask set in a heating mantle controlled by a Variac. Adjust the Variac so that the solution is kept at about 80° C. In one of the necks place a water condenser, in another neck a thermometer and in the third neck a removable ground glass stopper. This third neck is used for pipetting the salting agent. Bring salting agent to 110° C before pipetting it into the separatory funnel. At lower temperatures crystallization may occur occasionally at the stopcock of the separatory funnel.

Aluminum nitrate wash solution:	Add 100 ml of aluminum nitrate salting solution (B.P. 130° C) to 73 ml of distilled water and 4 ml of concentrated nitric acid.
Filter paper:	Whatman No. 30 or equivalent, 11 cm. circle.
Sodium carbonate:	Reagent Grade.
Sodium carbonate solution, 10%:	
Hydrogen peroxide solution 3%:	Dilute 10 ml of 30% Reagent grade hydrogen peroxide to 100 ml with distilled water.
Stopcock grease:	Silicone base.
Sodium fluoride C.P.:	This reagent is purchased in 100-lb. lots (about 4 months supply). At the order point (50 lb.) one pound samples representing as many production lots as the producer has on hand are ordered with the request that a 100-lb. lot of each be reserved. They are tested for pelletizing characteristics and for fluorescence under slow and hot fusing conditions* with and without standard uranium addition. A suitable batch is not too fluffy and gives a fairly solid pellet. With the 100-milligamma U_3O_8 standard aliquot, it will give a meter reading of 800 mm with the MIT instrument or 50 units with the Galvanek Morrison instrument, and blanks of 5 to 10 mm with the former and 1 to 2 units with the latter.
Sodium fluoride-lithium fluoride tablets:	Tablets composed of 98% sodium fluoride: 2% lithium fluoride have been made available commercially under the aegis of this Division, and their use is recommended.

* One batch of sodium fluoride was sent here for examination which gave 20% less fluorescence under hot fusion conditions than under cool conditions (fusion carried out just above the melting point) using pure uranium standards. Actual samples were scarcely affected at all, but since all samples are referred to standards fused at the same time, the net result was that under fast fusing conditions, the sample assays would be reported higher than was actually the case. It should be noted that all the samples in this case appeared visibly to be quenched (the beads were tinged and dull). Nevertheless it would appear wise to test the fluoride in use over a range of fusing conditions.

FLUORIMETER RECORDS PAGE NO.

LAB. NO.	SAMPLE	ASSAYS REQ'D	NO. OF DET.	RANGE	NO. OF ACIDS	DILUTIONS	FLUO. PAGE	ASSAY
1234	4-3-12 RES	U_3O_8		.03-.01	3	29 /500 mls	1500	0.015

FIGURE 20-FLUORIMETER LABORATORY RECORDS

SAMPLE RECORDS

Each sample is given a laboratory number which is taken consecutively from a master record. This number is then entered in the laboratory record book, a page of which is shown in Figure 20. The columns, whose headings are self-explanatory, are filled in as the sample progresses through the procedure.

A laboratory assay sheet, as shown in Figure 21 is prepared when the samples are diluted ready for the fusion step. One sheet is prepared for each set of samples, corresponding to a single fusion. This is usually four samples. The sample solutions in the glass stoppered bottles are handled in trays, and the assay sheet on which the sample numbers and dilution factors are recorded accompany them for the balance of the procedure.

FLUORIMETER LABORATORY PAGE: 1500

LAB NO.	DESCRIPTION	DILUT.	ALIQ.	GALV. READING		AVR.	BLK	U_3O_8	ASSAY	AV. ASSAY
1234	4-3-12 RESIDUE	29/500 mls	.06	200	190	195	185	34.6	.01444	0.015
			.1	340	310	325	315	58.9	.0147	
STANDARD: 100 mg U_3O_8			0.1	550	540	545	535			
			0.1	530	560					
STANDARD:										
BLANKS	10	10								

FINAL ASSAY REPORTED	
#1234	0.015
CALC. BY:	ENT. BY:

DIL. BY [illegible] PIPETTED BY [illegible] READ BY [illegible]

DATE ENTERED Feb 20/51 DATE READ Feb 21/51

REMARKS _____ PLATE NO. ____

FIGURE 21

FLUORIMETER LABORATORY ASSAY SHEET

PROCEDURE

a) Sample Preparation

Solids

Multi-acid Treatment

Weigh 1 or 2 grams of solid sample (all −150 mesh) depending on the uranium content (*see* Table 2B) and carefully transfer to a 250-ml Pyrex beaker which has been tested for strength by tapping. Moisten the sample with 2 or 3 ml of water. Add 10 ml of concentrated hydrochloric acid, cover the beaker and digest on the hot plate for 10 minutes. Add a few drops of hydrofluoric acid, cover and boil again.

Add 10 ml concentrated nitric acid, 5 ml of dilute (1:1) sulphuric acid and 5 ml of hydrofluoric acid. Place the uncovered beaker on the hot plate and evaporate to dryness.

Fume the dry sample over a gas flame (Meker burner) until all the dense white sulphuric anhydride fumes have disappeared. Cool, add 5 ml of concentrated nitric acid and rinse down the sides with about 50 ml of water. Cover the beaker and boil 10 minutes.

Nitric Acid Treatment

With many ores, the following treatment gives satisfactory results:

Weigh 1 or 2 grams of solid sample (all −150 mesh), (*see* Table 2B) and transfer to a 250-ml beaker. Add 40 ml of 1:1 nitric acid, cover with a watch glass and boil 10 minutes.

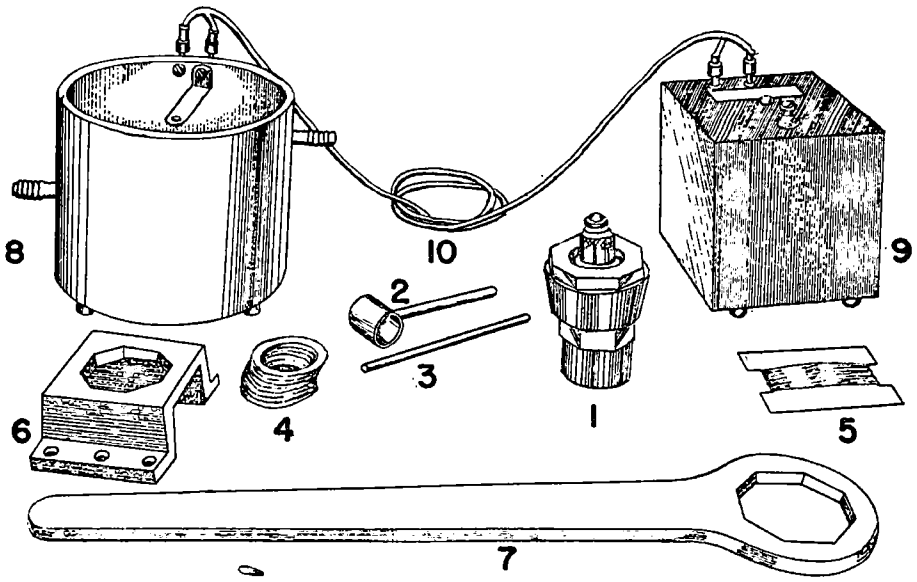
If this method is used routinely, it is essential that the feed and tailings samples be checked regularly by a total solution method (multi-acid or fusion).

Refractory Solids

Peroxide Sinter

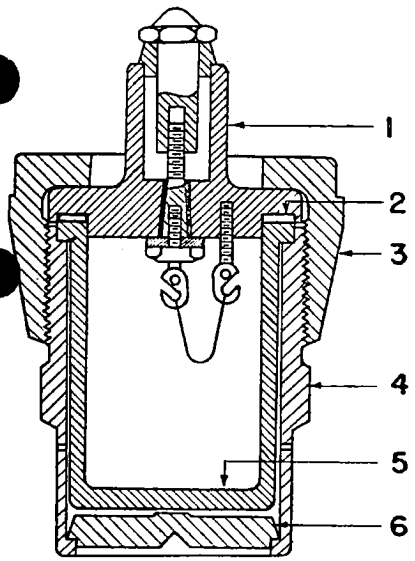
Transfer 0.2 to 1.0 gm of the sample ground to pass a No. 240 B.S. sieve to a 30-ml porcelain or nickel crucible and mix with 1 to 3 grams of sodium peroxide. Cover the crucible and place it on a silica plate in an electric muffle (a little back from the door) which is maintained at 480° ± 10° C (preferably by an automatic control). Leave the crucible for exactly 7 minutes, then remove it from the muffle.*

*The sinter may also be carried out at 400°C for 30 minutes to reduce attack on the crucible.

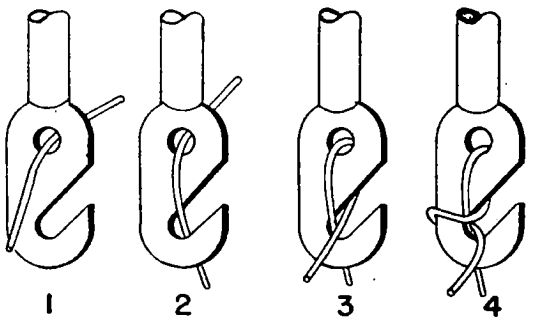


PEROXIDE BOMB APPARATUS

FIGURE 22



BOMB ASSEMBLY



METHOD OF ATTACHING FUSE WIRE

FIGURE 23

Let the crucible cool and transfer it to a 600-ml beaker. Cover with a smooth rimmed watch glass and cautiously add water in small amounts using a wash bottle. When the cake is disintegrated and cold, acidify the extract by carefully but rapidly adding a sufficient excess of nitric acid to give a solution containing 5-10% free acid (in this way precipitation of insoluble acids, which occurs if the neutral point is approached slowly, may be prevented).

Finally, add about 10 ml of hydrofluoric acid to convert the silica to the more easily filtered silicofluoride, boil to destroy peroxide, and filter. Any unattacked mineral should be recovered and treated again.

Parr Bomb Fusion

CAUTION: Wear glasses or goggles. Clean the cup, dry on a hot plate and cool on a metal block before use. All apparatus must be *clean and dry.* Never let moisture touch the charge (this includes perspiration from fingers or brow). Note particularly the precautions given in the Parr Manual, pp. 25, 26 (13).

Grind together an accurately weighed 0.5 to 2.0 gm portion of the sample (all minus 200 mesh) and 1.0 gm (weighed) of finely ground sugar-carbon. Transfer completely to a dry cup using a brush and immediately cover with a dry gasketted dust cover.

Prepare the electric ignition head by attaching a 7-cm length of fuze wire to the electrodes as shown in Figure 23. Pass one end of the wire through the eyelet of an electrode so that it will extend one-quarter of an inch. Tuck this

short end into the hook; wrap the free wire around the narrow portion formed by the neck of the hook; then make an additional turn to bind the short end. Pull the wire downward in line with the electrode and attach the free end of the wire to the other electrode in the same manner. Do not make the fuze loop too long. It should hang just above the surface of the charge.

When ready to assemble the bomb, add 1 dipper (15 gm) of sodium peroxide, cover immediately with the dust cover, and shake vigorously with a rolling motion for at least one minute.

Inspect the bell body (No. 4 Figure 23) to make sure all holes are open. Remove the dust cover and brush all adhering particles into the cup. Check the head gasket (No. 2 Figure 23) to make sure it seats properly. Seal the bomb by turning down the screw cap (No. 3 Figure 23), till it is finger-tight, then put it in the bench socket and tighten the screw cap firmly. Place the assembled bomb under the ignition contact arm in the water bath (No. 8 Figure 22). Make the necessary hose connections and fill the bath till the bomb is completely submerged. Make sure a continuous stream of cold water will flow through the bath during the ignition and cooling periods.

Attach the plugs on one end of the connecting cord (No. 10 Figure 22) to the two binding posts on the water bath. Connect the other end of the cord to the terminals on the ignition unit which are marked for use with a 7-cm fuze. Extend the cord so the ignition unit is a safe distance from the bomb. Ignite the charge by pressing the button and holding it until the pilot light stops glowing (not more than five seconds in any case). Let the bomb cool for 5 minutes and remove from the bath.

Dismantle the bomb and wash the head with hot distilled water, collecting the washings in a 600-ml beaker. Make the washings up to about 150 ml with more hot water, and using crucible tongs, put the cup into the beaker, covering it immediately with a smooth-rimmed watch glass. Dissolve the melt completely, warming if necessary when the action slows down. Remove the cup and wash with about 200 ml of hot distilled water.

Neutralize the solution carefully but rapidly with nitric acid, and add sufficient excess so that the final solution will be 5% in nitric acid. Add about 10 ml of hydrofluoric acid to convert the silica to silicofluoride. Boil to destroy peroxide and filter. Recover and fuse again any unattacked residue.

Pyrosulphate Fusion (Titanium, Niobium and Tantalum Present)

Transfer a 2-gm sample to a 60-ml Vycor crucible. Add about 15 gm of potassium pyrosulphate and fuse over a Meker burner with auxiliary air supply, gently at first until the reaction moderates. Heat for about 15 minutes, then raise the gas and increase the air to give a blast flame. Heat 15 minutes at the higher temperature. Let cool, transfer the crucible to a 400-ml beaker and dissolve the melt in 200 ml of water. Remove and wash the crucible, collecting the washings in the beaker. Boil the dissolved melt for 1½ hours to hydrolyze the earth acids. Transfer the solution and precipitate to the appropriately sized volumetric flask and dilute to volume (*with water only*). Mix well and let the precipitate settle completely. Filter a sufficient volume through a dry paper into a dry beaker, and from this, pipette the aliquot for the second dilution into a volumetric flask of the required size. Dilute to volume with 5% nitric acid and mix well.

Organic Liquid Samples

Decomposition with Acids

Pipette a suitable aliquot (*see* Table 2 A) into a 250-ml Erlenmeyer flask. Add 10 ml 1:1 sulphuric acid. Fume over a gas burner, swirling to prevent

spitting, and continue till the sample chars. Add concentrated nitric acid, 2 or 3 drops at a time, fuming and swirling after each addition until the black colour is all gone. Let cool, carefully dilute with about 10 ml of water and transfer to a 250-ml beaker. Take to dryness on a hot plate, and fume off the sulphuric. Take up in sufficient nitric acid to give a 5% concentration of the acid when diluted to the desired volume.

Pyrosulphate Fusion

Pipette a suitable aliquot into a 250-ml Erlenmeyer flask. Evaporate off the kerosene on a padded hot plate. Add 5 ml concentrated sulphuric acid and 1 or 2 grams of potassium pyrosulphate. Fume 2 or 3 minutes on the hot plate, then finish over a Meker gas burner until a clear colourless melt is obtained. Let cool, add 25 ml water and warm to dissolve. Add sufficient nitric acid to make the solution 5% when diluted to the desired volume.

Carbonate Fusion

Pipette a suitable aliquot (*see* Table 2) into a Coors No. 1A porcelain crucible. Insert a 1″ long piece of twisted filter paper ($\frac{1}{2}$″ wide) to serve as a wick. Place in a fume hood and ignite. Let burn until the organic matter is completely consumed and only carbon remains, (replace the wick if necessary). Finally burn off the carbon by putting the crucible in a hot muffle (400-900° C) for 2 or 3 minutes. Remove, cool and add 1 or 2 grams of sodium carbonate. Fuse over a burner for several minutes. Cool. Carefully add concentrated nitric acid to the crucible in 1- or 2-ml portions until there is no further reaction. Rinse into the appropriate sized volumetric flask using the stream from a wash bottle. Add sufficient excess nitric acid to give 5% in the final volume.

Extraction with Sodium Carbonate Solution

Pipette 25 ml of the organic sample into a 125-ml separatory funnel and shake for 1 minute with 50 ml of 10% sodium carbonate solution. Draw the aqueous layer into a beaker and wash the inside of the funnel stem into the beaker using a small amount of distilled water. Repeat the extraction with two 10-ml portions of the sodium carbonate solution. Carefully neutralize the solution with nitric acid and add sufficient excess to give a 5% concentration in the final volume.

Extraction with Nitric Acid (for Amine Extractants only)

Pipette 25 ml of the sample solution into a 60-ml separatory funnel. Add 10 ml of 5% nitric acid and shake for 30 seconds. Drain off the aqueous layer into a 250-ml beaker and rinse the stem of the funnel into the beaker with distilled water. Repeat the extraction with 10 ml of 5% nitric acid twice more. Dilute to the required volume with 5% nitric acid.

Solution Samples

All solution samples are treated in the same way as solid samples which have been brought into solution, except that the dilution table for solutions is used in place of the one for solids. Use 5% nitric acid for dilution.

If the solid sample, brought into solution by one of the above procedures, or the solution sample, as received, is known to be free from quenchers, proceed to following page "Dilution". If quenchers are known to be present remove them by the appropriate method in the following.

b) Removal of Quenchers

Removal of Interfering Manganese

Add 50 ml of concentrated nitric acid to the beaker containing the sample solution in 5 or 10% nitric acid. Stir and add solid sodium chlorate in 0.5-gram portions boiling between each addition. (One or two additions should be sufficient). Proceed with the "Dilution" step.

Ethyl Acetate Extraction

Dilute the sample solution obtained above to a suitable volume in a volumetric flask, making the solution 5% in nitric acid. (If two dilutions are being made, this will correspond to the first dilution). Pipette a suitable aliquot (e.g. the volume required for later dilutions, if two dilutions are called for, i.e. 5 or 10 ml) into a 100-ml beaker. If the sample is in the range where only one dilution would be carried out, choose aliquots and dilutions to give a final solution in the same concentration range as for untreated samples. In no case take more than 10 ml for extraction. Add 3 drops of 3% hydrogen peroxide and warm the beaker. Transfer the solution in the beaker to a 60-ml separatory funnel,* (the stopcock of which has been lubricated with silicone grease) using an equal volume of 5% nitric acid to rinse the beaker. Add by means of a graduated pipette, 6.5 ml of aluminum nitrate (at 110° C) per 5-ml volume of combined sample and rinse volume. Cool the solution to room temperature and add 20 ml of ethyl acetate (this can be used to first rinse the beaker). Stopper the separatory funnel with a polyethylene or pretreated rubber stopper. Shake the funnel for 45-60 seconds. If crystallization takes place in the separatory funnel near the stopcock, place the lower part of the funnel in a beaker of hot water until the solidified portion dissolves.

After the layers have separated, drain off and discard the aqueous (lower) layer. Do not drain off any cloudiness which appears at the boundary in the funnel. Rinse inside the stem of the separatory funnel with a stream of water from a wash bottle and discard the rinsing.

Add 15 ml of water to the separatory funnel containing the ethyl acetate, stopper the funnel and shake the mixture for about 1 minute. After washing off the stopper with water, drain the aqueous layer into a volumetric flask of suitable size (Table 2). Wash the separatory funnel and ethyl acetate layer four or five times with 5-ml portions of water by means of a wash bottle, and add the washings to the volumetric flask.

Removal of Thorium (Thorium Concentrates)

To the sample solution, volume about 150 ml and all uranium oxidized to UO_2^{++}, add 10 drops of concentrated hydrofluoric acid for each gm ThO_2. Boil, cool, and dilute as described. Filter or centrifuge a portion and aliquot as required.

c) Dilution

Following the ethyl acetate extraction procedure just described, the sample will have been diluted to the proper range.

In the case of samples which required no treatment (the bulk of the samples received) and the filtrates from the manganese removal step, transfer the complete sample including any solid residue, and the required amount of nitric acid to make the final volume 5% in this acid, to the appropriate size volumetric flask (*see* Table 2) and add tap water to fill up the body of the flask. Mix, let the contents of the flask come to room temperature and make to the exact

* Funnels with Teflon stopcock plugs, which require no lubrication, are now available.

volume. (Time required for this step can be reduced if a large carboy or aspirator bottle of water, fitted with a siphon and quick-fill valve (e.g. Crane No. 432, ½″ brass) is used and the bottle filled each night so that it will be at room temperature.) Mix the contents of the volumetric flask thoroughly and let settle.

If two dilutions are required, aliquot from this flask to a second volumetric flask of the proper size, add 5 ml concentrated nitric acid for each 100 ml of volume and again dilute to the mark at room temperature. Regardless of previous treatment, decant 10 or 20 ml of the final dilution through an 11-cm Whatman No. 3 filter paper into a glass-stoppered, 30-ml, wide-mouth bottle. Take the completed assay sheet for each group of samples and place the sheet and the samples that it covers, on a tray for transfer to the pipetting room.

d) Aliquotting the Samples into the Platinum Dishes

Lay out the set of clean dishes (22 in all) on the tray (Figure 24) using platinum-tipped forceps. Place the tray in the infra-red drier for several minutes.

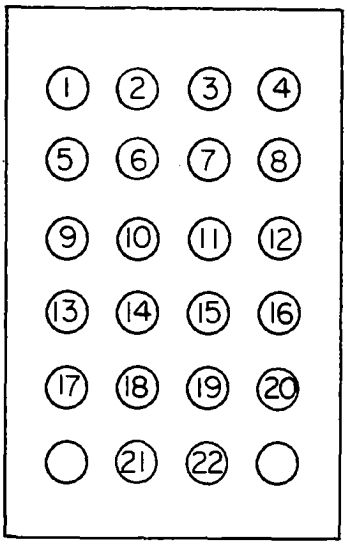


FIG. 24—ORDER OF DISHES IN TRAY

Table 2

A—Dilution for Solution Samples

Range gm/l	Dilution orig. vol. to dil. vol.	Factor 0.05 ml	Factor 0.10 ml
<0.001	none	2×10^{-5}	1×10^{-5}
0.001-0.005	10/50	1×10^{-4}	2.5×10^{-5}
0.005-0.02	10/100	2×10^{-4}	1×10^{-4}
0.02-0.03	10/250	5×10^{-4}	2.5×10^{-4}
0.03-0.06	5/250	1×10^{-3}	5×10^{-4}
0.06-0.12	5/500	2×10^{-3}	1×10^{-3}
0.12-0.03	5/1000	4×10^{-3}	2×10^{-3}
0.3-0.7	2/1000	1×10^{-2}	5×10^{-3}
0.7-1.5	2/2000	2×10^{-2}	1×10^{-2}
1.5-3.0	5/500 × 5/100	4×10^{-2}	2×10^{-2}
3.0-6.0	5/1000 × 5/100	8×10^{-2}	4×10^{-2}
6.0-15.0	5/1000 × 5/250	2×10^{-1}	1×10^{-1}

Table 2—Concluded

B—Dilution for Solid Samples

Range %	Dilution orig. wt. to dil. vol.	Factor 0.05 ml	Factor 0.10 ml
0.001-0.002	5/100	4×10^{-5}	2×10^{-5}
0.002-0.005	1/50	1×10^{-4}	5×10^{-5}
0.005-0.01	1/100	2×10^{-4}	1×10^{-4}
0.01-0.03	1/250	5×10^{-4}	2.5×10^{-4}
0.03-0.06	1/500	1×10^{-3}	5×10^{-4}
0.06-0.1	1/1000	2×10^{-3}	1×10^{-3}
0.1-0.3	1/500 × 5/25	5×10^{-3}	2.5×10^{-3}
0.3-0.6	1/500 × 5/50	1×10^{-2}	5×10^{-3}
0.6-1.2	1/500 × 5/100	2×10^{-2}	1×10^{-2}
1.2-2.5	1/1000 × 5/100	4×10^{-2}	1×10^{-2}
2.5-6.0	1/1000 × 5/250	1×10^{-1}	5×10^{-2}
6.0-10.0	1/1000 × 5/500	2×10^{-1}	1×10^{-1}
10.0-25.0	0.5/1000 × 10/1000	4×10^{-1}	2×10^{-1}
25.0-70.0	0.3/1000 × 10/1000	6.6×10^{-1}	3.3×10^{-1}
70.0-100.0	0.3/1000 × 5/1000	1.32×1	6.6×10^{-1}

Table 3

Wide Range Dilutions for Rapid Approximate Analysis of Solutions

Range gm/l	Dilution	Factor 0.05 ml	Factor 0.10 ml
less than 0.2	2/250	2.5×10^{-4}	1.25×10^{-4}
0.2 to 0.6	2/1000	1×10^{-3}	5×10^{-4}
above 0.7	2/2000	2×10^{-3}	1×10^{-3}

Remove the tray of dishes from the drier and let it cool. (Never stack the trays on top of one another.) Using a rubber bulb to draw up the solution, pipette the samples onto the dry dishes using a clean 0.3-ml pipette (or a 0.2-ml pipette, if these are not available) graduated in 0.05-ml divisions, for each sample. In pipetting, let the bulk of the solution run into one corner of the dish, then stop the flow at the desired mark, and touch the tip of the pipette to a dry corner of the dish to remove the small drop adhering to the tip. Note particularly that the solution level in the pipette does not drop down below the mark in doing this. If there is a tendency for solution to creep up the outside of the pipette, it can be corrected by occasionally wiping the tip with a Dow-Corning "Sight-Saver" (silicone impregnated tissue).

Pipette two 0.05-ml aliquots and two 0.10-ml aliquots from the same sample, one aliquot to each of four dishes. Proceed in the same manner for four samples to each set of 22 dishes, using 16 of the dishes. Then in four of the remaining dishes pipette 0.10 ml of the standard uranium solution, (i.e. 100 mγ U_3O_8). Use the middle row of four dishes for these standards (*see* Figure 24). Finally leave the last two dishes (the last row) with no solution, for use as blanks.

This is the general procedure. However for samples where only an approximate answer is required, or a large throughput of samples is needed, only two aliquots may be pipetted. On the other hand, for composite head and tailing

samples or in other cases where higher accuracy is required, two determinations are usually made (8 beads) on each of two trays (i.e. two separate fusions are used.)

Use of Micropipettes

If the highest accuracy is required, pipette one complete set of dishes per sample, using a 100γ micropipette throughout, and alternating sample and standard solution (i.e. pipette every other dish with the sample, then rinse thoroughly and pipette the standard in the intervening dishes with the same pipette). Rinse the micropipette with the solution before pipetting and rinse with 1:1 hydrochloric acid followed by distilled water, before putting it away. Use of a single volume of solution presumes that no quenching will occur. Return the tray of dishes containing the samples and standards to the infra-red drying oven and let them dry slowly so that they do not spit. Take particular care with samples that have been taken into solution by fusion methods since due to their high salt content they tend to decrepitate, spoiling both the samples themselves and adjacent samples. Turn down the Powerstat control when drying these samples.

Remove the tray of dry dishes to the fluoride dispensing fume hood and dispense a pellet of sodium fluoride (from a pelletizer which has been adjusted to deliver a 0.7 ± 0.25 gram pellet) into each dish. Alternatively, use a pre-formed mixed flux tablet. Transfer the tray to the fusion fume hood.

Using the platinum-tipped forceps, remove the dishes from the tray and arrange them on the burner according to a scheme similar to that shown in Figure 25.

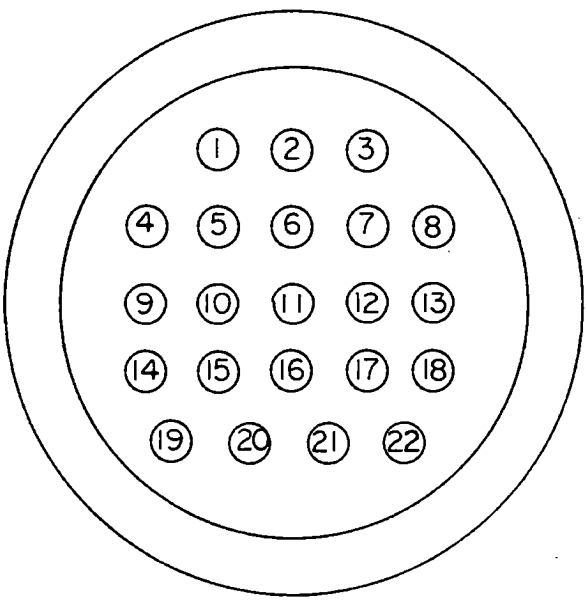


FIGURE 25

ORDER OF LAYING OUT DISHES ON BURNER

e) The Fusion (using the burner with vacuum cleaner air supply)

Turn on the gas and ignite it by means of the pilot light. Adjust the gas flow to give a reading on the manometer which has been found to give satisfactory fusing conditions (*see* APPARATUS: The Gas Burner and Its Adjustment).

Turn on the air supply and adjust the needle valve on the gas supply until the burner begins to "howl", then increase the gas flow just enough to prevent howling.

If the conditions are correct, the pellet will melt in about 1½ minutes. The melting time is checked by means of a stopwatch. Continue the fusion for another 1½ minutes timed by the stopwatch.*

While the sample is fusing, turn on the electric steam generator. When the fusion time is complete, shut off the gas and air and immediately play a jet of steam (vapour) over the burner and the beads until the beads no longer glow red.

Remove the dishes from the burner with the platinum-tipped forceps and replace them in the tray in their proper order. Let the beads cool to room temperature and read them on the fluorimeter.

f) Fluorimeter Operation—MIT Model 3

Turn on the blower and cooling water to the instrument. Make sure the shunt is at its highest setting. Turn on the power supply and the ultra violet lamps. Let the instrument warm up for 15-20 minutes. While waiting, check the bead holder to make sure it is clean and free from fluorescent material. After the warm-up period, move the glass standard into the reading position and adjust the voltage output of the power supply to give a suitable galvanometer deflection (800 mm is used at the Mines Branch). Using the platinum-tipped forceps, transfer the dishes to the bead holder of the instrument and record the readings (i.e. the product of the shunt factor and the galvanometer reading in millimeters) in the space provided on the assay sheet which accompanies the tray. Check the standard again when the complete set has been read.

g) Fluorimeter Operation—GM Fluorimeter

Place the 100 mγ (white) standard in the standard position. This is done by removing the front stop and drawing out the sample slide to expose the standard position at the rear, inserting the standard and replacing the slide as before.

Plug the power supply into the back of the instrument by means of the two six-prong plugs on the ends of the power supply cables. Connect the line power to the back of the instrument by means of the four-prong plug, and connect the fused plug to a source of 110 volts 60 cycle A.C. Turn the coarse voltage control and fine voltage control fully counter-clockwise. Switch the instrument on by means of the "on-off" switch and allow it to warm up 15 minutes. Pull the slide out to the front stop (positioning the standard under the phototube). Zero the microammeter by depressing the zero switch and adjusting the zero control knob. Switch the coarse voltage control to increase the voltage applied to the phototube until the microammeter reads from 30 to 40 microamperes.

Adjust the reading of the microammeter to read 500 by means of the fine control.

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* A modification which appears to eliminate bubbles in the beads is as follows:
Continue as usual to the asterisk. Then increase the gas flow slightly to give a large cooler flame for 30 seconds or till the bubbles disengage. Return to the recommended flame conditions for another 30 seconds and proceed as described above.

Re-zero the microammeter, then re-adjust the coarse and fine voltage controls to give a microammeter reading of 500. Repeat these two adjustments until the meter reads zero when the zero switch is depressed and 500 when it is up, without further adjustment of the controls.

If the instrument has a dark current suppression control, this is now adjusted. Push the empty sample slide in and press the 0.001 multiplier switch. Adjust the dark current control until the microammeter again reads zero. The background reading should remain constant during the day. Any change is usually due to contamination and should be corrected by cleaning rather than by adjusting the dark current control.

Withdraw the sample holder slide again. Using the platinum-tipped forceps, insert the sample bead in the sample position and move the slide all the way in (placing the sample bead under the phototube).

Note the microammeter reading and close successive multiplier switches from right to left until the maximum reading that is still on scale is obtained.

Check the zero and full scale readings before measuring the fluorescence of each bead. Always observe the recommended order of use for the multiplier switches to avoid damage to the meter.

Record the microammeter reading on the form which accompanies the set. The reading obtained is the product of the microammeter reading and the multiplier switch used to obtain it.

Alternative procedure

The following revised procedure speeds up the reading of fluorescence considerably and is based on the observation that the instrument is as stable as the fluorescence output of the standard phosphor, and that voltage adjustments are sometimes made as a result of faulty operating technique rather than because of instrument fluctuation.

Remove the 100 mγ (white) standard from the standard position. This is done by lifting out the front stop, drawing out the sample slide to expose the standard position at the rear, removing the standard, and replacing the slide as before. The former standard position (i.e. slide fully out) is now used for dark current adjustment.

Plug the power supply into the back of the instrument by means of the two six-prong plugs on the ends of the power supply cables. Connect 110 volt 60 cycle line power to the back of the instrument by means of the four-prong plug cord. Turn the coarse voltage control and fine voltage control fully counter-clockwise. Switch the instrument on by means of the "on-off" switch and allow it to warm up 15 minutes. Pull the slide out to the front stop and place one of the regular standard beads (containing 100 mγ U_3O_8) in the sample position. With the slide out or in, zero the microammeter by depressing the zero switch and adjusting the microammeter. (It will be noted that with the slide pulled out, the 0.01 multiplier is automatically in the circuit and it is necessary to press the zero switch to cause the microammeter needle to move away from zero. With the slide in, the 10 multiplier is automatically in the circuit and the needle moves almost as far as it does with the zero switch down. It will therefore speed up routine reading if the zero is adjusted with the slide pushed in. No error or harmful effect to the instrument results from this practice.)

With the slide in (i.e. with the sample position, containing the standard bead, under the photocell), close the 0.01 multiplier switch, and adjust the coarse and fine voltage controls until the microammeter reads about 50 microamperes.

Re-zero the microammeter, then re-adjust the coarse and fine voltage controls to again give a reading of 50 microamperes.

If the instrument has a dark current suppression control this is now adjusted. Pull the slide out, positioning the empty standard position under the photomultiplier and adjust the dark current control until the microammeter reads zero. It is not necessary to close any of the shunt switches since pulling out the slide automatically puts the instrument on the 0.01 multiplier. (More sensitivity in setting the dark current can be obtained by the previous method, where it was possible to use the 0.001 multiplier switch. This switch cannot be used in the revised procedure but the sensitivity is adequate.)

With the sample slide out, insert the sample bead in the sample position, using the platinum-tipped forceps. Move the sample slide in (placing the sample bead in the sample position) and note the microammeter reading. When the slide is in, the microammeter is automatically connected through a current-limiting resistor which reduces the current through the meter by a factor of 10, and the reading obtained can be multiplied by 10. Close successive multiplier switches from right to left until the maximum reading that is still on scale is obtained. Record the microammeter reading on the form which accompanies the set of beads. The reading obtained is the product of the microammeter reading and the multiplier switch used to obtain it.

At the same time, note the zero reading. With the slide in, the zero reading can simply be noted and adjusted, without closing any of the switches, as already discussed.

Pull the slide out to remove the bead that has been read, and insert the next bead. At the same time note the dark current reading, and adjust if necessary. Once again, no switches need be closed.

Continue reading the beads and checking the zero and dark current. After the instrument is once adjusted it should not be turned off, or the voltage changed, without restandardizing. The zero or dark current may have to be adjusted slightly from time to time, but any major movement from the zero position should be thoroughly investigated.

When finished reading for the day, turn the line switch off, and leave the sample slide (empty) pushed in to the sample position, since this leaves the current-limiting resistor in the microammeter circuit and may provide a measure of protection for it.

Further information on the fluorimetric determination of uranium using the GM Fluorimeter will be found in references (11), (12) and (14).

CALCULATIONS

Solid Samples

$$\%\ U_3O_8 = \frac{\text{1st dil'n (ml)}}{\text{sample wt.}} \times \frac{\text{2nd dil'n}}{\text{1st dil'n aliq.}} \times \frac{\text{m}\gamma\ U_3O_8 \text{ in bead}}{\text{2nd dil'n aliq.}} \times \frac{100}{10^9}$$

Solution Samples

$$\text{gm/l } U_3O_8 = \frac{\text{1st dil'n (ml)}}{\text{sample aliq.}} \times \frac{\text{2nd dil'n}}{\text{1st dil'n aliq.}} \times \frac{\text{m}\gamma\ U_3O_8 \text{ in bead}}{\text{2nd dil'n aliq.}} \times \frac{1000}{10^9}$$

The factor 10^9 converts mγ to grams.

"mγ U_3O_8 in bead" is found from

$$\frac{(\text{R sample} - \text{R blank})}{(\text{R 100 m}\gamma\text{ standard} - \text{R blank})} \times 100$$

where R is the galvanometer reading.

Carry out a calculation on each of the four values obtained, the two on the 0.05-ml aliquot and the two on the 0.10-ml aliquot. If the average of the results from the 0.10-ml aliquot is significantly (i.e. more than 10% of the value obtained) lower than that from the 0.05-ml aliquot, the fluorescence is probably being quenched. In this case, rerun the sample, using a greater dilution if the uranium content was high, or an ethyl acetate extraction if the value was low. Otherwise report the result as the average of the four values. Do not report more than two significant figures, since the reproducibility of the method is not sufficient to warrant a third figure.

If the galvanometer reading for a sample is not more than twice the reading for the blank, the amount of uranium should be reported as "less than" the minimum amount detectable at the dilution used, rather than using the term "not detected". This value may be taken as 2 mγ in the sample bead, and the result may be reported as "less than" the concentration corresponding to this figure, using the method of calculation given above.

Rapid Method of Calculation

Instead of calculating each result individually, the table of factors given for the various dilutions may be used (Table 2). In this case determine the "mγ in the bead" and multiply this by the factor to obtain the assay.

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The Determination of "Secondary" Uranium: Carbonate Leach-Fluorimetric Method

METHOD U-2

SCOPE

This method is intended to provide a rough estimate of altered uranium products in ores (a) as an indication of whether the ore is of surface or underground origin, and (b) as an indication of possible losses in hydraulic ("gravity") separation processes. (Secondary uranium minerals are, as a rule, more friable and water soluble than the primary minerals.) It is also useful for examining residues from acid leach processes to determine whether poor recovery is due to incomplete leaching, or is caused by reprecipitation of uranium during the leaching and filtering steps.

RANGE

The lower limit of determination is the same as for the fluorimetric method ($1 \times 10^{-4}\%$ U_3O_8) and the method can be used up to about 0.5% of "secondary" uranium (as U_3O_8).

OUTLINE

The method is based on the observation that sodium carbonate solution containing no added oxidizing agent will readily dissolve certain altered uranium materials, while not attacking pure pitchblende appreciably (1). Addition of a small amount of bicarbonate is necessary to prevent re-precipitation of sodium diuranate.

The method has been investigated using mixtures of pure pitchblende with synthetic uranyl arsenate and phosphate precipitates, and using the New Brunswick Laboratory carnotite standards. It is believed that it will distinguish such primary uranium minerals as pitchblende, uraninite, and the niobate-tantalate-titanate minerals, from secondary arsenate, carbonate, molybdate, phosphate, vanadate, and sulphate minerals, and from oxide and silicate minerals when uranium is present in its higher (+6) valence state. About 5 to 10% of the uranium content of ores from the Bancroft area reports as "Secondary Uranium" by this procedure. The proportion is higher in ore from the Blind River area (up to 25%) and in ores from the Beaverlodge area (up to 50%).

APPARATUS

Casseroles:	Coors size 3A, 210 ml capacity.
Watch glasses:	115 mm dia.
Buchner funnels:	Coors size No. 2.
Suction flasks:	250 ml size.
Filter paper:	Whatman No. 1, 7 cm dia.
Beakers:	250 ml.
Dispensing burette:	250 ml size.
Volumetric flasks:	Various sizes.

REAGENTS

Sodium carbonate-bicarbonate solution: 90 gm anhydrous sodium carbonate, 10 gm sodium bicarbonate per litre distilled water.

Nitric acid, concentrated:

PROCEDURE

Weigh a 2-gm sample of the ore into a size 3A casserole. Add 50 ml of Na^2CO_3–$NaHCO_3$ solution from a dispensing burette. (A larger or smaller sample may be used, but the ratio of 25 ml of solution per gm of sample should be adhered to.) Cover with a watch glass and let boil gently on a padded hot plate for 30 minutes (exactly), maintaining the volume at 50 ml by adding water, if necessary.

Filter on a Whatman No. 1 filter paper (use two if necessary) on a Buchner funnel using suction. Cautiously neutralize with nitric acid in the suction flask, and add sufficient excess nitric acid to give a 5% concentration in the final dilution. Transfer to a volumetric flask of appropriate size and dilute according to the table in METHOD U-1. Complete the determination according to the procedure given in that method (2, 3).

CALCULATIONS

Calculations are carried out as described in METHOD U-1.

If the final reading is of the same order as the blank, the result shall be reported as "less than" the limit of detection, an actual figure based on the sample weight taken and the dilution used. Details for this reporting are also given in METHOD U-1. The result is reported as % Soluble U_3O_8 (CO_3'' leach).

References

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3. METHOD U-1.

The Colorimetric Determination of Uranium Using Tributyl Phosphate and Ethyl Acetate Extraction

METHOD U-3

SCOPE

This method is to be used for the determination of small amounts of uranium in ores and solutions. It is intended for use as an alternative to the fluorimetric method (7) for uranium in cases where values by an independent method are required, or where the necessary equipment for fluorimetric assay is not available. The separations given may also be used to purify grossly impure samples for fluorimetric analysis.

RANGE

The range of the method is considered to be from 0.005 to 1.0% or gm/l U_3O_8. It may be extended to smaller amounts by using 5-cm cells in the spectrophotometer.

OUTLINE

Uranium is separated from contaminants by means of an ethyl acetate extraction from a nitric acid solution heavily salted with aluminum nitrate (1, 2, 3). If the uranium content of the sample is very low a preliminary extraction of uranium is carried out using a solution of tributyl phosphate in n-hexane from a strong nitric acid solution (4), to separate uranium from the bulk of the impurities, which otherwise tend to cause formation of emulsions during the ethyl acetate extraction. Final determination of uranium is carried out colorimetrically either by the sodium hydroxide-hydrogen peroxide method, by the thiocyanate method (4, 5, 6), or by the fluorimetric method (7).

APPARATUS

Beckman DU spectrophotometer with 1 cm or 5 cm Corex cells:	
Separatory funnels, (Squibb, pear shaped):	60 ml, 125 ml.
No. 0 stoppers:	Either polyethylene or rubber. If rubber is used boil twice in ethyl acetate for 10 minutes.
Heating mantle:	Similar to Ace 6478.
Reaction flask (1000 ml):	Similar to Ace 6476, 6486.
Water condenser:	

REAGENTS

Aluminum nitrate salting solution: Place approximately 450 gm of reagent grade (Mallinckrodt) aluminum nitrate ($Al(NO_3)_3 \cdot 9\ H_2O$) in a 600-ml beaker and add 25-30 ml of distilled water. Cover the beaker and heat the mixture on a hot plate until a clear solution is obtained. Remove the cover glass and concentrate the solution by boiling until a boiling point of 130° C is reached. Transfer to a 1000-ml three-neck reaction flask set in a heating mantle. Adjust the heating so that the temperature of the solution is kept about 80° C. In one of the necks place a water condenser, in another neck a thermometer and in the third neck a removable ground glass stopper. This third neck is utilized for pipetting the salting agent. It is recommended that the salting agent be brought to a temperature of 110° C or more before pipetting it into the separatory funnel. If the salting agent is added at a lower temperature, crystallization may occur occasionally at stopcock of the separatory funnel. If the solution is to stand overnight, unheated, add 35 ml water per 100 ml solution and mix well.

Aluminum nitrate wash solution: Add 100 ml of aluminum nitrate salting solution (B.P. 130° C) to 73 ml of distilled water and 4 ml of concentrated nitric acid.

Ethyl acetate (Merck, reagent grade):

Hydrogen peroxide, 30% (reagent grade):

Standard uranium solutions: Dissolve appropriate quantities of pure uranium oxide of known U_3O_8 content in 1:1 nitric acid and make the solutions up to volume in appropriate volumetric flasks. The final acidity of the uranium solutions should be 5% in nitric acid. Make up the solutions so that 1 ml will contain from 0.1 mg to 1.0 mg U_3O_8. If necessary, dry the uranium oxide standard at 105° C for 24 hours before weighing, or carry out a moisture determination and correct the values of the standard solutions accordingly.

Sodium hydroxide, 20% solution: Dissolve 200 gm of sodium hydroxide in distilled water and make up to 1000 ml with distilled water.

Tributyl phosphate in n-hexane, 22%: Dilute 22 ml of tributyl phosphate to 100 ml with n-hexane.

Sodium hydroxide 20%-hydrogen peroxide 1% solution: Add 1 ml of 30% hydrogen peroxide to 99 ml of 20% sodium hydroxide solution.

Ammonium thiocyanate solution, 50%: Dissolve 50 gm ammonium thiocyanate in distilled water, filter, and adjust the volume to 100 ml. Make the solution up fresh daily.

Stannous chloride solution, 10%: Dissolve 10 gm of stannous chloride in 10 ml concentrated hydrochloric acid by warming on a hot plate. Cool and dilute to 100 ml with distilled water. Make the solution up fresh daily.

Sulphuric acid dil.: 1:1 (v/v).

PROCEDURE

Assay samples containing less than 0.1% or 0.05 gm/l uranium oxide by a procedure using a tributyl phosphate extraction and an ethyl acetate extraction, followed by a colorimetric finish using either the sodium hydroxide-hydrogen peroxide procedure (if thorium is absent) or the thiocyanate procedure in the presence of thorium. On samples containing greater than 0.1% or 0.05 gm/l U_3O_8, omit the tributyl phosphate step. The tributyl phosphate step alone can be used to purify samples for the fluorimetric method, U-1.

Solid Samples

Weigh out an appropriate quantity (1-10 gm) of sample into the balance pan and transfer to a 250-ml beaker. Boil the sample with 20 ml of 1:1 hydrochloric acid in a covered beaker for 10 minutes. Remove the cover glass and add 10 ml of nitric acid, 5 ml of perchloric acid and 10-20 ml of 1:1 sulphuric acid. If necessary, add a few ml of hydrofluoric acid. Finally fume the sample to dryness and leach the residue with 10% nitric acid. If an ethyl acetate extraction only is to be carried out, transfer the solution and residue to an appropriate volumetric flask, adjust the acidity to 5% in nitric acid, and make to volume. Transfer a suitable aliquot (*see* APPENDIX) directly to a 60- or 125-ml separatory flask and proceed at once with the ethyl acetate extraction.

If the sample grade is less than 0.1% or 0.05 gm/l, a preliminary tributyl phosphate extraction is required. Leach the residue with 5 N nitric acid and filter the precipitate through a Whatman No. 3 filter paper using a Buchner funnel. Wash the paper and precipitate three times with 5 N nitric acid.

Tributyl Phosphate Extraction

Transfer the filtrate and washings to a separatory funnel with 5 N nitric acid and add 50 ml of 22% tributyl phosphate solution for every 100 ml of sample solution. Stopper the funnel with a ground glass stopper and mix for 3 minutes. Drain off the aqueous layer into a separatory funnel, and repeat the extraction with a second 50-ml portion of the tributyl phosphate solution. Discard the aqueous layer. Combine the organic layers. Strip the uranium from the combined organic layers with one 10-ml and one 5-ml portion of a mixture of 20% sodium hydroxide and 1% hydrogen peroxide, and wash twice with 5-ml portions of water. (*Caution*: The mixture evolves gas. Relieve pressure frequently!) Collect the strippings in a 60- or 125-ml separatory funnel. Acidify with nitric acid, and add 1 ml of concentrated nitric acid in excess. Adjust the volume to 20 ml. Carry standards through the procedure in the same manner as the samples. Complete either by the following procedure, or by METHOD U-1.

Ethyl Acetate Extraction

Add, by means of a graduated pipette, 6.5 ml of aluminum nitrate per 5 ml of sample solution. Cool. Add 10-20 ml of ethyl acetate and shake the mixture for 1 minute. Stopper the funnel with a polyethylene stopper. Drain off and discard the aqueous layer. Do not discard the cloudy portion which may appear at the boundary between the organic and aqueous layers. Add 10 ml of aluminum nitrate wash solution to the funnel and shake the mixture for 1 minute. Drain off and discard the aqueous layer, once again being careful to retain the cloudy portion which may be present at the boundary between the aqueous and organic layers. Repeat this washing procedure. Finally rinse out the inside of the stem of the separatory funnel with a stream of water from a wash bottle.

Water Stripping of Uranium from the Ethyl Acetate Layer followed by the Sodium Hydroxide-Hydrogen Peroxide Colorimetric Finish (to be used if thorium is absent)

Add 10 ml of distilled water to the separatory funnel containing the ethyl acetate, stopper the funnel and shake the mixture for about 1 minute. After washing off the stopper with water, drain the aqueous layer into a volumetric

flask of suitable size. Repeat the water stripping operation, again using 5 ml of distilled water. Combine the aqueous fractions.

On samples which are very low in uranium content (less than 0.005 gm/l or % U_3O_8) use the following procedure: Evaporate the water strippings to dryness on a hot plate, add 10 ml of 20% sodium hydroxide-1% hydrogen peroxide solution and warm until complete sample dissolution. Read the cooled solution directly on the spectrophotometer in the manner described above.

Otherwise add 10 ml of 20% sodium hydroxide and 0.25 ml of 30% hydrogen peroxide per 25 ml final volume. Make the solution up to volume with distilled water. Mix and read the absorbance after 15 minutes on the Beckman DU spectrophotometer at 370 mμ against a blank which has been carried through the extraction. Compare the absorbances of the samples against a standard curve or against the absorbances of standard uranium solutions which have been carried through the procedure at the same times as the samples.

Water Stripping of the Uranium from the Ethyl Acetate Layer followed by the Thiocyanate Colorimetric Finish (to be used if thorium is present)

Add 5 ml of distilled water to the separatory funnel containing the ethyl acetate, stopper the funnel and shake the mixture for about 1 minute. After washing off the stopper with water, drain the aqueous layer into a volumetric flask of suitable size. Repeat the water stripping operation, this time using 5 ml of distilled water. Combine the aqueous fractions.

Neutralize the solution with dilute sodium hydroxide solution, add dilute hydrochloric acid until the precipitate just dissolves, and then add 2.5 ml of 20% hydrochloric acid in excess per 25 ml final volume. Add 0.5 ml of 10% stannous chloride solution and 7 ml ammonium thiocyanate solution per 25 ml final volume. Dilute to the mark with distilled water and allow the colour to develop for 15 minutes. Read the absorbance on the Beckman DU spectrophotometer at 370 mμ against an extraction blank. Compare the absorbances of the samples against a standard curve or against the absorbances of standard uranium solutions which have been carried through the procedure at the same time as the samples.

Solution Samples

If a tributyl phosphate extraction is necessary, take an appropriate aliquot of a solution sample, neutralize with dilute sodium hydroxide solution and adjust the acidity to 5 normal with nitric acid. Continue with a tributyl phosphate extraction as for solid samples.

If a tributyl phosphate extraction is not necessary, take an aliquot of the solution sample, add 5 drops of concentrated nitric acid per 5 ml of sample solution and continue with an ethyl acetate extraction as for solid samples.

CALCULATIONS

Solids

$$\%\ U_3O_8 = \frac{\text{mg } U_3O_8 \text{ per 25 ml (from graph)}}{1000} \times \frac{\text{sol'n vol.}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

Solutions

$$\text{gm/l } U_3O_8 = \frac{\text{mg } U_3O_8 \text{ per 25 ml (from graph)}}{1000} \times \frac{1000}{\text{aliquot taken}}$$

If the sample gives approximately the same reading as the reference solution, the amount of U_3O_8 shall be reported as "less than" the minimum amount detectable, (an actual figure based on the sample weights and volumes used). The minimum amount detectable may be taken as 0.20 mg per 25 ml volume for the hydrogen peroxide colour and 0.10 mg per 25 ml volume for the thiocyanate colour using 1-cm cells. As an example, the figure to report for a solid sample in the latter case would be

$$\%\ U_3O_8 = \text{less than } \frac{0.10}{1000} \times \frac{\text{solution volume}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

APPENDIX

Suggested Choice of Sample Size and Procedure

(1-cm cells—Sodium Hydroxide-Hydrogen Peroxide finish—25 ml vol.*)

Range gm/l or % U_3O_8	Sample wt. or aliq. gm or ml	Dil. ml	Tributyl phosphate +ethyl acetate extractions	Ethyl acetate extractions
<0.03%	10 gm	—	√	—
0.03–0.06%	5 gm	—	√	—
0.06–0.10%	2 gm	—	√	—
0.10–0.30%	10 gm	250/25	—	√
0.30–0.60%	5 gm	250/25	—	√
0.60–1.0%	2 gm	250/25	—	√
<0.03 gm/l	100 ml	—	√	—
0.03–0.05 gm/l	50 ml	—	√	—
0.05–0.12 gm/l	25 ml	—	—	√
0.12–0.30 gm/l	10 ml	—	—	√
0.30–0.60 gm/l	5 ml	—	—	√
0.60–0.10 gm/l	2 ml	—	—	√

* As the sensitivity of the thiocyanate finish is approximately double that of the sodium hydroxide-hydrogen peroxide finish, the above values should be corrected accordingly if the former finish is being used. The table above is designed to detect, where possible, 1.0–3.0 mg U_3O_8 in 25 ml volume. This range gives absorbance readings between approximately 0.200–0.650 using the Beckman DU spectrophotometer and 1 cm cells, with the sodium hydroxide-hydrogen peroxide colorimetric method.

References

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7. METHOD U-1.

The Determination of Uranium in Uranium Concentrates and Solutions Using Ethyl Acetate Extraction and the Hydroxide-Peroxide Colorimetric Finish

METHOD U-4

SCOPE

This method is to be used for uranium determination on uranium products and concentrates and on high-grade uranium solutions. The fluorophotometric method, METHOD U-1 should be used for uranium determinations on low-grade uranium ores and solutions.

RANGE

Uranium determinations on solid samples containing greater than 5% uranium oxide and solution samples containing greater than 1 gm/l uranium oxide are carried out by this method.

OUTLINE

Uranium is extracted by means of ethyl acetate from a nitric acid solution of the sample, using aluminum nitrate as a salting agent. After water stripping of the uranium from the organic layer, final determination is carried out colorimetrically by the sodium hydroxide-hydrogen peroxide method (1).

The uranium nitrate molecule forms complexes which are designated solvates, with many oxygen-containing organic compounds. Ethyl acetate is one such compound. The reaction is believed to be

$$UO_2^{++}\ \text{aq.} + 2NO_3^{-}\ \text{aq.} + 2(\text{Et O Ac})\ \text{org.} \longrightarrow UO_2(NO_3)_2 \cdot 2(\text{Et O Ac})\ \text{org.}$$

The solvated complex is more soluble in the organic layer than in the aqueous layer. The mechanism of the extraction process has been elucidated in detail by Mackay and others (2-7).

The solubility of the solvated complex is enhanced by the presence in the aqueous layer of "salting" agents and in the method described, a saturated solution of aluminum nitrate is used for this purpose. It acts in a number of ways to accomplish this. An increase in nitrate ion concentration tends to depress the ionization of uranyl nitrate, and promotes formation of the solvated complex. High concentration of nitric acid, however, results in extraction of other metal nitrates. The use of aluminum nitrate provides a high concentration of nitrate ions without leading to high hydrogen ion concentrations. It serves

to bind water molecules (as a result of the tendency of aluminum to form hydrolysis compounds) and in this way reduces the concentration of "free" water available to form "aquo" complexes and aqueous solutions of the uranyl nitrate. Aluminum is also effective in forming complex compounds with phosphate, arsenate, fluoride and sulphate which would otherwise complex the uranium and prevent its extraction. The extremely high solubility of aluminum nitrate in water and the fact that it does not interfere in the peroxide-hydroxide or thiocyanate colorimetric procedures nor in the fluorimetric method are also highly desirable properties.

Theory of Solvent Extraction

If a solute is shaken with two immiscible solvents, and its molecular state is the same in both, then at any given temperature

$$\frac{\text{The concentration of solute in solvent A}}{\text{The concentration of solute in solvent B}} = \frac{C_A}{C_B} = E_B^A \text{ (a constant)}$$

E_B^A is known as the *partition coefficient.*

The significance of this insofar as the present method is concerned, is that if we can extract a certain amount of uranium from the aqueous solution by using an equal volume of ethyl acetate, we do not extract twice as much by doubling the volume of ethyl acetate and leaving the volume of the aqueous phase the same. Instead, very roughly, we halve the concentration of the uranium remaining in the aqueous layer. To illustrate, suppose the extraction coefficient of the present system is $E_a^o = 50$, and we are extracting 11.5 ml of aqueous solution with 20 ml ethyl acetate. If the aqueous layer contains 0.020 gm U_3O_8, we can determine the amount remaining after one extraction as follows. Let the amount (wt in gm) remaining in the aqueous layer be X_1. Its concentration will be $X_1/11.5$. The amount in the organic layer will be $0.020-X_1$, and the concentration in the organic layer will be $\frac{0.020-X_1}{20}$.

Then from the Distribution Law,

$$\frac{\frac{0.020-X_1}{20}}{\frac{X_1}{11.5}} = 50$$

Solving for X_1, we get

$$X_1 = 0.00022 \text{ gm}$$

The amount in the organic layer will therefore be 0.01978 gm i.e. 98.9% extraction.

Then if we take instead 40 ml ethyl acetate, it will extract 0.019943 i.e. 99.4% extraction.

If instead we perform a second extraction with 20 ml ethyl acetate, the distribution will be expressed by

$$\frac{\frac{0.00022 - X_1}{20}}{\frac{X_1}{11.5}} = 50$$

$$X_1 = 0.0000025 \text{ gm}$$

i.e. the amount extracted is 0.0199975 gm
or 99.99% extraction.

The above discussion is not strictly valid, since as we have seen, the species extracted is actually solvated uranyl nitrate. We have assumed in the above discussion, therefore, that this is the only species present. Actually we may expect that this compound will dissociate to some extent in the aqueous phase and that the equilibrium involved will be somewhat more complicated than is indicated here (8).

In the regular procedure one extraction only is employed, and standards carried through the extraction procedure are used to correct for incomplete extraction.

In the differential procedure, a double extraction is employed, since, as we have seen, this is more efficient than a single extraction using twice as large a volume of ethyl acetate, and complete recovery is of course more important in this case.

The actual partition coefficient for this extraction does not appear to have been determined. However, recent studies in this laboratory and elsewhere (9) have shown that 20 ml of ethyl acetate will quantitatively remove in one extraction up to 200 mg of U_3O_8 from 11.5 ml of a solution 2.5% in nitric acid containing about 10 gm of aluminum nitrate enneahydrate. This uranium is quantitatively stripped from the ethyl acetate solution with water.

Extraction of Impurities

Grimaldi and Levine investigated the extraction of thorium, zirconium, vanadium, iron and aluminum. Of these, only thorium was appreciably extracted, E_a^o, being $\doteq 1.5$ (12). Guest (1) confirmed this, and also investigated the extraction of molybdenum, copper, arsenic, phosphorus, cobalt, calcium, magnesium and manganese, none of which were extracted. He also investigated the interference of the above elements and of cerium (III), nickel and chromium in the overall method:—no interference was found. In the case of cerium (III) this means none was extracted. The extraction of cerium was also investigated by Zimmerman and Guest (11).

In the absence of the salting agent the uranyl nitrate is readily back-extracted from the ethyl acetate into water

Colorimetric Finish

Final determination of the uranium is carried out colorimetrically, using the colour developed when sodium hydroxide and hydrogen peroxide are added to the solution of uranyl nitrate in water.

The literature on the alkaline peroxide colorimetric finish has been admirably summarized by Rodden (12). The colour is not intense, so that this is not a very sensitive method, but it is extremely reproducible and is stable for at least 12 hours provided that ions causing catalytic decomposition of peroxide are absent.

There are a number of interferences, most of which are removed by the ethyl acetate extraction procedure described above. Of the anions, chloride, nitrate and sulphate do not interfere. Phosphate above 10 gm/l, silicate above 0.6 gm/l and fluoride above 0.1 gm/l cause bleaching of the colour (13). Chromate interferes seriously and vanadium exhibits a similar effect. It has been shown that the interference due to vanadium in the sodium hydroxide-peroxide system can be eliminated by boiling and cooling the solution (14).

This is not part of the present procedure, but should be borne in mind in the event that extremely high vanadium material is encountered at some time. Normally vanadium gives a colour equivalent to about an equal amount of uranium at 370 mμ.

Manganese interferes by occluding and absorbing uranium, and by catalyzing decomposition of the peroxide. Iron behaves similarly, but to a lesser extent. Large amounts of copper and nickel cause low results due to occlusion and even trace amounts cause very rapid decomposition of the peroxide. This peroxide decomposition may so reduce the peroxide concentration as to cause low results, but the principal objection is to the presence of gas bubbles in the solution, which makes it difficult to get an accurate reading of the optical density of the coloured compound.

Molybdenum interferes slightly, but the interference can be greatly reduced by letting the solution stand 4 hours. (It should be noted that molybdenum interferes very seriously in the thiocyanate colorimetric procedure, so that this is the method of choice if molybdenum is present.)

Calcium, magnesium, cerium, and thorium precipitate. They may be removed by centrifugation, but the latter two may occlude uranium. Thorium is the only one of these not removed by the ethyl acetate extraction, and for determination of uranium in thorium-bearing material, the thiocyanate method is recommended.

This method includes a description of a modification which permits the assay of high-grade uranium concentrate with a coefficient of variation of about 0.1%, for umpire purposes. Other important samples can also be handled expeditiously and accurately using this modification. The theory is discussed in detail in the early part of this manual and in some of the references (15-20). A simple example to illustrate the increase in accuracy that is possible, is all that is needed here.

Suppose that we can determine the uranium content of a solution containing 0.0200 gm U_3O_8 in 250 ml of final solution with a standard deviation (σ) of 0.00005 gm by ordinary colorimetry (i.e. using a spectrophotometer on which we have set the optical density scale at zero using a blank solution of the reagents, free of uranium).

If now, we wish to use the differential or high precision procedure, we choose instead a sample which will provide us with a final solution containing (let us assume, in this particular case), 0.1300 gm U_3O_8 in 250 ml. We then read this solution on the same spectrophotometer, but instead of setting the optical density at zero using a blank solution, as before, we use a standard solution of uranium containing exactly 0.1100 gm U_3O_8 in 250 ml. Read in this way, our sample solution, containing 0.1300 gm U_3O_8, will give the same optical density scale reading as 0.020 gm gave by regular colorimetry (assuming the uranium-sodium hydroxide-peroxide colour system shows no Beer's Law deviation, which seems to be the case). The reading will therefore fall in exactly the same place on the scale as before, the error in reading will be the same, and assuming no other sources of error, we may expect the same standard deviation, 0.00005 gm. The *relative error* (coefficient of variation) i.e. the standard deviation expressed as a percentage of the mean, is quite different in the two cases. By regular colorimetry, the coefficient of variation is $\frac{0.00005}{0.020} \times 100$, or 0.25 %. Using differential colorimetry, it becomes $\frac{0.00005}{0.130} \times 100$ or 0.04%. This is a sixfold reduction in error, and since the standard deviation, is a measure of the expected

error of a single determination, the relative error can be further reduced by replication, since the standard deviation of the mean of n observations is given by $\frac{\sigma}{\sqrt{n}}$. That is to say, the standard deviation of the average of four determinations will be half that of a result based on one determination. It is interesting to note that 36 replications would be necessary, employing regular colorimetry, to obtain the reduction in error achieved by a single determination using the differential procedure.

This discussion applies only to the precision of reading the spectrophotometer and the overall error of the method will be greater than is indicated here. In actual practice, an overall coefficient of variation of 0.18 has been obtained by the differential procedure, compared to a value of 0.46 by regular colorimetry.

It has been found that changes in temperature affect the results obtained, so a water-cooled lamp housing is used, and the cell compartment is maintained at room temperature by circulating water through two water jackets ("thermospacers") on each side of it. A set of *closely matched* cells is reserved for this procedure, and standard solutions, carried through the method, are read in the same cells as the samples, which reduces the necessity for path-length corrections. Cell corrections are nevertheless determined and are applied to the reading. The theory of the cell correction procedure is discussed in the early part of the manual. The volumetric glassware, especially the pipettes used, should be of the type constructed according to the U.S. National Bureau of Standards specifications, (Kimble Normax or equivalent) and should be calibrated as it will be used. (These pipettes differ from routine pipettes in having longer drainage time to reduce "hold-up" or drainage errors) (21).

In extremely warm weather, dilutions should be carried out at a standard temperature (say 25° C) using a water bath.

APPARATUS

Nickel crucibles:	50 ml capacity.
Nickel crucible covers:	to fit 1/8 in. hole in centre.
Fume traps:	glass, special design, *See* Figure 1.
Cooling rack and tray:	*See* Figure 1.
Wick, heavy cord:	saturate with 25% KNO_3 and let dry in a clear place.
Heating mantle:	sim. to Ace 6478.
Reaction flask (1000 ml):	sim. to Ace 6476, 6486.
Water condenser:	
Separatory funnels, Squibb pear-shaped:	60 ml and 120 ml sizes (funnels with Teflon plugs are available and do not require lubrication).
Rubber stoppers, No. 0:	(for the separatory funnels) Boil twice in ethyl acetate, 10 minutes each time.
or	
Polyethylene stoppers, No. 1:	Fisher Cat. no. 14-645.
Pipettes:	5, 10 and 15 ml sizes.

Pipettes, high precision: Normax or equivalent, 5, 10, 15, 20 and 25 ml (for high precision colorimetry).

Volumetric flasks: 25, 50 and 100 ml.

Volumetric flasks, Giles: 500-550 and 1000-1100 ml.

Volumetric flasks, Normax: 200, 250, 500 and 1000 ml.

Spectrophotometer, Beckman Model DU: (with 1 cm. cell compartment, No. 2360 water-cooled light housing, cooled directly by tap water, and two No. 2021 water-cooled thermospacers through which water at room temperature is circulated).

Water reservoir: Large polyethylene or glass carboy containing water at room temperature for circulation through the thermospacers by a small centrifugal pump.

Cells, spectrophotometric: 1-cm, two matched sets (one set reserved for high precision spectrophotometry).

REAGENTS

Aluminum nitrate salting solution: Place approximately 1500 gm of reagent grade (Mallinckrodt) aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) in a 2-litre beaker and add 80-150 ml of distilled water. Cover the beaker and heat the mixture on a hot plate. If a clear solution does not result after 5-10 minutes boiling, add 60 ml of water and continue the boiling for 5 more minutes. Repeat this step until a clear solution is obtained after boiling. Remove the cover glass and concentrate the solution by boiling until a boiling point of 130°C is reached. This makes about 1 litre (1060 ml) of solution, and 6.5 ml is equivalent to 9 gm Al $(NO_3)_3 \cdot 9H_2O$. Cover the beaker with a watch glass and either transfer the solution to a constant temperature apparatus or keep the solution warm, finally heating to about 110°C before use. If the solution is allowed to cool to approximately 60°C, recrystallization of aluminum nitrate will take place. It is necessary, therefore, to dilute the salting agent solution by about one-third in order to prevent recrystallization if the solution cools to room temperature. Accordingly, if the solution is to stand overnight, add 35 ml of distilled water per 100 ml salting agent solution, mix well and cover.

If the salting agent solution is to be stored, the following procedure has been found convenient:—adjust the solution to the proper concentration (B.P. 130°C) and transfer to a 1000-ml three-neck reaction flask set on a heating mantle. Adjust the heating so that the temperature of the solution is kept at about 80°C. In one of the necks place a water condenser, in another neck a thermometer and in the third neck a removable ground glass stopper. This third neck is utilized for pipetting the salting agent. It is recommended that the salting agent be brought to a temperature of 110°C before pipetting it into the separatory funnel. At lower temperatures crystallization may occur occasionally at the stopcock of the separatory funnel. (*See* METHOD U-1 for detailed apparatus list.)

Aluminum nitrate wash solution: Add 100 ml of aluminum nitrate salting solution (B.P. 130°C) to 73 ml of distilled water and 4 ml of concentrated nitric acid.

Sodium hydroxide solution, 20%: Dissolve 400 gm of reagent grade sodium hydroxide in distilled water and dilute to 2 litres.

Hydrogen peroxide, 30%, (reagent grade):

Ethyl acetate (Merck, reagent grade):

Nitric acid, dil.: 1 : 1 (v/v).

Hydrochloric acid, dil.: 1 : 1 (v/v).

Sulphuric acid, dil.: 1 : 1 (v/v).

Nitric acid, 5%:	Dilute 50 ml of concentrated nitric acid to 1000 ml with distilled water.
Nitric acid, 10%:	Dilute 100 ml of concentrated nitric acid to 1000 ml with distilled water.
Hydrofluoric acid (48%):	
Uranium oxide:	Standard MSST uranium oxide, 99.93% U_3O_8, or equivalent.
Standard uranium solutions:	Dissolve appropriate quantities of MSST uranium oxide or laboratory Secondary Standard in 1:1 nitric acid and make the solutions up to volume in appropriate volumetric flasks. The final acidity of the uranium solutions should be 5% in nitric acid. Make up the solutions so that a 5-ml aliquot will contain from 2-100 mg uranium oxide. Carry out a moisture determination on the MSST uranium oxide and correct the values of the standard solutions accordingly.

Preparation of Standard Spectrophotometric Calibration Curve

Prepare three calibration curves, one at 370 mμ and two at 400 mμ, using unextracted aliquots of the standard uranium solution. For the curve at 370 mμ, use standards covering the range 10 to 30 mg U_3O_8 in 250 ml final volume. To the aliquots contained in 250-ml volumetric flasks, add enough 20% w/v sodium hydroxide solution to neutralize the solution. Add 25 ml in excess, then add 2.5 ml 30% hydrogen peroxide and make up the volume to the mark with distilled water. Read the absorbance after 20 minutes, using the Beckman DU spectrophotometer at 370 mμ against a reagent blank, using 1-cm Corex cells and a slit width of 0.2 mm.

Similar curves are drawn up at 400 mμ, using (a) standards covering the range 10-60 mg U_3O_8 and (b) standards covering the range 110 to 150 mg, using the differential method and reading against the 110 mg standard as zero.

These curves, which need be prepared only once or twice a year, are used primarily to verify that reasonably quantitative extraction is being obtained. This is a convenience in preventing the possibility of errors due to abnormally low extraction, or due to otherwise undetected trouble with the reagent blank.

PROCEDURE

a) Preliminary Treatment

Port Hope Umpire Samples

Assay samples of about 10 gm each are prepared at Port Hope and are supplied in three screw-cap vials with the whole cap sealed with sealing wax. One vial only is used for assaying by this method.

Immediately prior to weighing the sample, remove the sealing wax carefully and completely without disturbing the screw-cap. Weigh the vial, including cap and contents, carefully on the analytical balance. Remove the cap and transfer the sample carefully to a 400-ml beaker (avoiding dusting, and the transfer of any loose sealing wax).

Reweigh the cap and the vial immediately, using forceps, if convenient, and avoid unnecessary handling. (Note that it is not necessary to transfer any small amount of sample adhering to the vial.) The difference in weight is the true weight of sample taken.

Dissolve the sample completely, and dilute according to its uranium content, using the dilutions and aliquots given in Table 3.

Other Chemical Concentrates for Accurate Regular or High Precision Assay

Preliminary Examination—Examine the samples carefully to ensure that they have been properly ground. Any samples that appear to have an appreciable quantity of +100 mesh material should be returned to the sample section for regrinding.

Rolling—Roll the sample for 30 minutes on the Kendall mixer, removing and shaking two or three times during this interval. Use a bottle that is not more than half full. If the sample bottle is too full for proper agitation, transfer the complete contents to a properly labelled, dry bottle of the right size and seal tightly. It has been recommended that solid high-grade samples of about 8 ounces in weight, properly ground, and packed in tightly sealed 16-ounce bottles should be provided to the laboratory in order to eliminate handling prior to rolling.

Uranium Assay and Moisture Determination—Place approximately 5 gm of the sample into a single, tared, wide-mouth, glass-stoppered weighing bottle that has previously been dried at 105° C and cooled to room temperature in a desiccator. At the same time, place the approximate amount required for the uranium assay (*see* Table 3) in each of two small, glass-stoppered, tared weighing bottles for each method of analysis being used and stopper the bottles immediately. These latter bottles should be dry ones that have been allowed to come to equilibrium with the atmosphere in the balance case, then tared. Carry out the entire operation as rapidly as possible, and then close the original sample bottle tightly. Weigh all the sample bottles, and deduct the tares of the bottles to arrive at the sample weight.

Place the wide-mouthed moisture dishes in a drying oven at 105° C. Remove the bottles from the oven at 24-hour intervals until no further loss in weight occurs. Calculate moisture as a percentage of the original weight.

b) Sample Solution

Solid Samples

Weigh out an appropriate sample (*see* Table 1). Umpire samples should first be handled as described above. Bring the sample into solution in one of three ways:—(1) single acid treatment, (2) multiacid treatment and (3) sugar carbon-sodium peroxide fusion.

Single Acid Treatment

Boil the sample in a covered 400-ml beaker for 20-30 minutes with 40 ml 1:1 nitric acid. Add 50 ml of water and boil the sample for 10 minutes more before transferring the solution and insoluble residue to an appropriate volumetric flask. Cool and make up to volume after adjusting the acidity of the solution to approximately 5% in nitric acid. Regulate the dilution so that the aliquot chosen for extraction will contain between 10 mg and 30 mg of uranium oxide if the final dilution for the colorimetric finish is to be 250 ml (*see* Tables 1, 2 and 3).

Multiacid Treatment

If the sample appears to be incompletely decomposed by nitric acid treatment, add 5 ml of hydrochloric acid, 5 ml of perchloric acid and 10 ml of 1:1 sulphuric acid. If it is considered desirable, add a few ml of hydrofluoric acid. Fume the sample to dryness and leach the residue with 25 ml of 1:1 nitric acid. Finally transfer the solution and residue to an appropriate volumetric flask and adjust to 5% in nitric acid as in the single acid treatment.

Sugar Carbon-Sodium Peroxide Fusion

CAUTION: Explosive mixture, WEAR SAFETY GLASSES

The procedure of Muehlberg (22) may be used. Transfer a 0.5-gm sample and 0.5 to 0.7 gm of sugar carbon to a 60-ml nickel crucible. Counterpoise the crucible on the balance pan and add 15 gm sodium peroxide. Mix. Tamp the mixture with a glass stopper, cover and place the crucible in a rack in a cooling bath. Through the hole in the crucible cover, place the tip of 4 inches of wick, the end of which has been lit and is at a glow. Quickly cover with the glass fume trap (Figure 1). When cool, tap the crucible sharply and transfer the melt to a dry, covered 600-ml beaker. Add water cautiously until the first violent reaction has ceased. Slowly add nitric acid until the solution is acid and then add enough nitric acid in excess so that the final volume of solution is 5% in nitric acid.

The procedure used at the Mines Branch is as follows:—Grind 1 gm of ore and 1 level spoonful (2 cm wide) of sugar carbon in a mortar. Place the mixture in a 60-ml nickel crucible, add 6 level spoonsful of sodium peroxide and mix thoroughly. Tamp with a glass stopper and continue as above.

The above procedure may also be carried out using the Parr bomb, if this is available. The procedure will be found in METHOD U-1.

Solution Samples

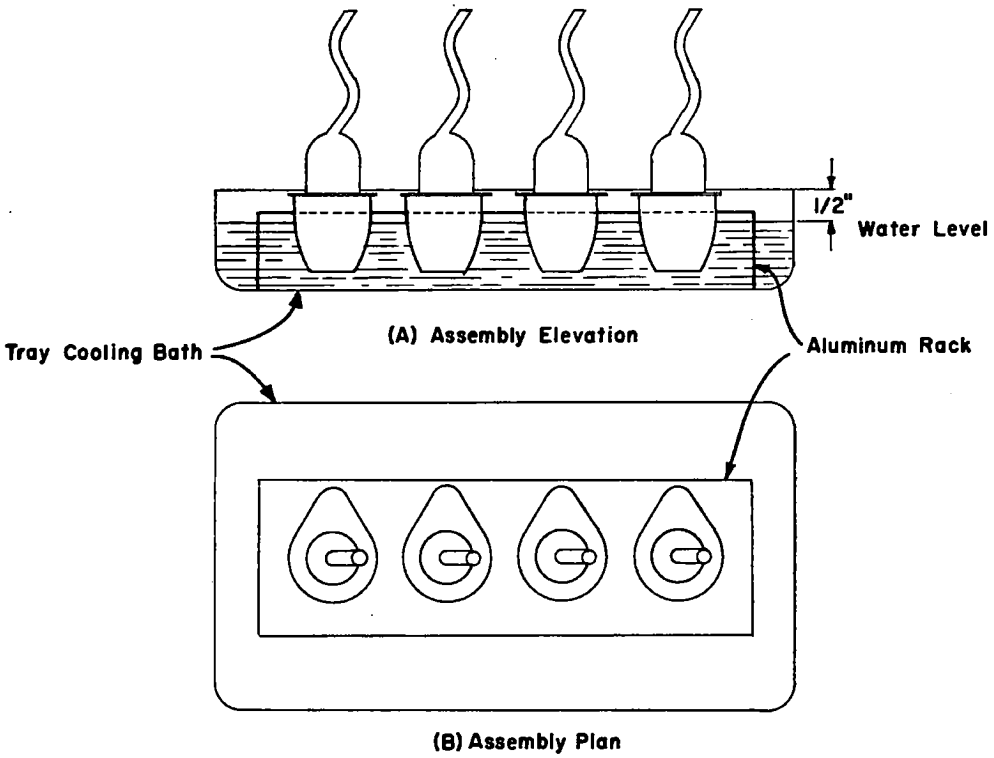
Aliquot solution samples directly or dilute as required (*see* Table 2), for an ethyl acetate extraction. If the sample is aliquotted directly for an extraction, add 5 drops of concentrated nitric acid per 5-ml aliquot of sample and standards before extraction. Where samples are diluted before aliquots are taken for extraction, adjust the acidity so that the final volume is 5% in nitric acid.

Organic Extractants

Organic solutions, principally 5 to 10% solutions of branched long-chain aliphatic amines or phosphate esters in kerosene, varsol, Stoddard solvent or VMP naphtha are used as extractants for uranium, and samples for analysis contain 0.1 to 10 gm/l U_3O_8. If the type used is known, it can often be stripped by a specific aqueous strip solution, some of which are described in METHOD U-1.

If this information is not available, or in preliminary test work, destroy the organic material completely by the following procedure.

Take a sample containing about 20 mg U_3O_8 (not more than 15 ml at a time, in any case) and transfer it to a 250-ml Erlenmeyer flask. Add 10 ml 1:1 sulphuric acid. Heat the flask directly over a Meker burner, swirling to prevent spitting, until the organic matter is charred. Cool slightly, add nitric acid, two or three drops at a time, and fume over the burner again. Repeat the nitric acid addition and the fuming till the solution is free of charred material and is completely clear. Cool, add 10-15 ml of water cautiously and transfer completely to a 250-ml beaker, rinsing the flask with a wash bottle. Take to dryness on a hot plate, fume off the sulphuric acid, and take up in 10 ml nitric acid and 10 ml water. Evaporate to about 5 ml, transfer completely to a 60-ml separatory funnel, using about 10 ml of wash water. Add about 20 ml of salting agent (6.5 ml per 5 ml of final solution) and proceed with the extraction.



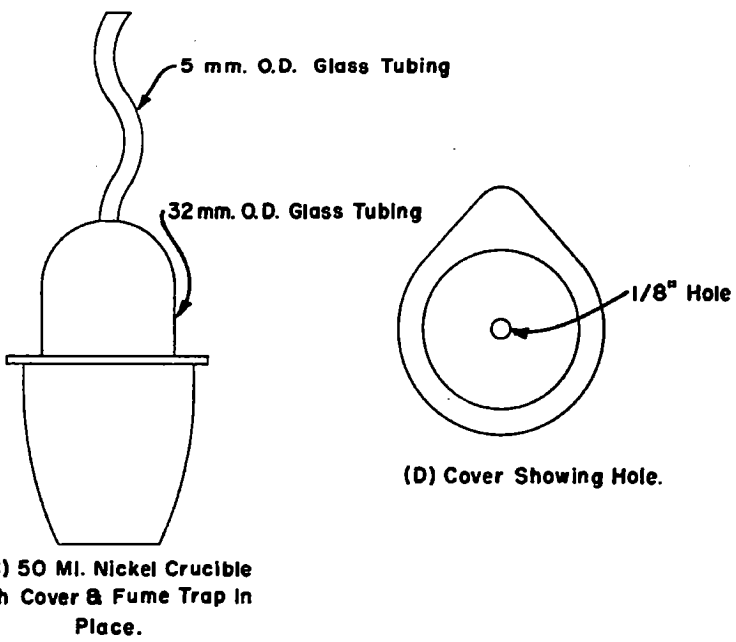


FIG. 1 – APPARATUS FOR SUGAR CARBON FUSION.

Other Methods of Dissolving Samples

Other procedures for dissolving samples which provide solutions suitable for this procedure will be found in METHOD U-1.

The Ethyl Acetate Extraction

Place an appropriate aliquot (usually 5 ml) containing 10 to 30 mg uranium oxide into a 60-ml separatory funnel, the stopcock of which has been lubricated with silicone grease.* At the same time, pipette into similar funnels aliquots of the standard arunium solutions covering the same range of concentrations as the samples being analyzed, using a ratio of about one standard for every six samples. Add, by means of a graduated pipette, 6.5 ml of aluminum nitrate solution per 5 ml of sample solution. The aluminum nitrate salting solution should be added while hot (greater than 110° C). Cool the solution to room temperature and add 20 ml of ethyl acetate. Stopper the separatory funnels with pretreated rubber stoppers. Shake the mixture for 45-60 seconds. Occasionally, crystallization may take place in the separatory funnel near the stopcock. In such a case place the lower part of the separatory funnel into a beaker of hot water until the solidified portion dissolves.

After the layers have separated, drain off the aqueous (lower) layer. Occasionally a cloudiness will appear at the boundary of the aqueous and organic layers. This cloudy portion should *not* be drained off. Add 10 ml of aluminum nitrate wash solution to the funnel and again shake the mixture for 45-60 seconds. Drain off the aqueous layer, once again being careful to retain the cloudy portion at the boundary in the funnel. Rinse inside the stem of the separatory funnel with a stream of water from a wash bottle.

Water Stripping of Uranium from the Ethyl Acetate Layer followed by the Sodium Hydroxide-Hydrogen Peroxide Colorimetric Finish (Thorium Absent)

Add 15 ml of water to the separatory funnel containing the ethyl acetate, stopper the funnel and shake the mixture for about 1 minute. After washing off the stopper with water, drain the aqueous layer into a volumetric flask of suitable size and wash the separatory funnel and ethyl acetate layer four or five times with 5-ml portions of water by means of a wash bottle. Combine the aqueous fractions.

Add enough 20% sodium hydroxide solution (w/v) to neutralize the solution and dissolve any precipitated aluminum hydroxide, then 10 ml in excess per 100 ml final volume. Add 1 ml of 30% hydrogen peroxide per 100 ml final volume and make up the volume to the mark with distilled water. Read the absorbance after 20 minutes on the Beckman DU spectrophotometer at 370 mμ against a reagent blank, using 1-cm Corex cells and a slit width of 0.2 mm. Compare the absorbances of the samples against the absorbances of the standard uranium solutions which have been carried through the procedure at the same time. The final volume for colorimetric reading is usually 250 ml for 10-30 mg of uranium oxide.

Water Stripping and Colour Development, Thorium Present, (The Removal of Interfering Thorium)

After an ethyl acetate extraction, water strip the uranium from the ethyl acetate and collect the uranium fraction in a 250-ml beaker. Add enough 20%

*Separatory funnels with Teflon stopcock plugs are now available.

(w/v) sodium hydroxide solution to neutralize the solution and redissolve precipitated aluminum hydroxide. Then add 10 ml excess of 20% sodium hydroxide solution and 1 ml of 30% hydrogen peroxide per 100 ml final volume. Filter the solution through an 11-cm 41H filter paper (Whatman), collecting the filtrate in a volumetric flask of suitable size. Wash the paper and precipitate once with 5 ml of a solution of 2% sodium hydroxide containing 0.1 ml of 30% hydrogen peroxide. Redissolve the precipitate by washing the paper with 10 ml of 10% nitric acid solution, collecting the washing in the original beaker. Neutralize the solution with 20% sodium hydroxide solution and add 2 ml in excess. Add 0.5 ml of 30% hydrogen peroxide and filter off the precipitate on the original filter paper, washing as before and collecting the filtrates in the original volumetric flask. If the precipitate on the paper is coloured yellow this step should be repeated. Make the solution in the volumetric flask up to volume and read the absorbance on the spectrophotometer. Carry standards through the same procedure as the samples.

Double Extraction of Uranium with Ethyl Acetate followed by Application of High Precision Colorimetry (Differential Working)

Uranium determinations requiring the highest accuracy may be carried out by a double extraction or uranium with ethyl acetate followed by the application of differential colorimetry as described by Hiskey and others (2, 3, 4, 6). In such a case it is recommended that between 100 and 150 mg of uranium oxide be extracted and a wave length of 400 mμ be used during the colorimetric finish. The procedure described below has been found satisfactory.

Pipette an aliquot of sample solution containing 110 to 150 mg uranium (*see* Table 3) into the 60-ml separatory funnels, using Normax or equivalent recalibrated pipettes.

Normally, this aliquot should be 10 ml. If, due to the difficulty sometimes experienced in getting a suitable dilution, a larger aliquot must be taken, pipette it into a 50- or 100-ml beaker, evaporate to 5 ml and transfer quantitatively to the separatory funnel. Rinse the beaker with water and then with the salting solution to obtain quantitative transfer. Alternatively, use 120-ml separatory funnels for the extraction.

At the same time, pipette into similar funnels aliquots of the standard uranium solution containing 110, 130, 140 and 150 mg U_3O_8. Adjust the volumes of salting solution, and extract with 20 ml of ethyl acetate as in the regular procedure, above.

Draw off the aqueous layer into a second separatory funnel containing 10 ml of ethyl acetate. Stopper the funnel and shake the mixture for 45-60 seconds. Drain off and discard the aqueous layer. Add 10 ml of aluminum nitrate wash solution to the first ethyl acetate extract, stopper and shake the mixture for 45-60 seconds. Drain off the aqueous layer into the separatory funnel containing the second ethyl acetate extract, stopper and shake the mixture for 45-60 seconds. Drain off and discard the aqueous layer. If the sample is highly contaminated, this step should be repeated. Combine the ethyl acetate fractions. Rinse the second separatory funnel with 20 ml of water, draining the washings into the separatory funnel containing the combined ethyl acetate fractions. Shake the mixture for 1 minute. Continue the water stripping as described above, collecting the fractions in an appropriate volumetric flask. Finish colorimetrically as described previously, allowing the strongly coloured solution to stand 1 hour to 2 hours to ensure stability before reading, as a fading effect of about 0.005 absorbance units has sometimes been noted on freshly prepared samples.

Read the absorbance of the sample solution on the Beckman DU spectrophotometer at 400 mμ against the reference solution which contains a known amount of uranium and has been carried through the extraction and colour development procedure in the same manner as the sample.

Read the other standards, containing slightly higher and lower amounts of uranium than the sample. Determine the cell correction by one of the methods described below.

Cell Corrections (Approximate Method)

Fill all four cells with the reference solution most closely approximating the sample solutions. Set the absorbance scale at zero with the reference cell in the light path, then read the absorbances of the cells used for the samples. Designate these absorbances as "+" or "−" depending on whether they lie above or below zero. These are the correction factors. Subtract them from all readings made in the respective cells (i.e. subtract positive absorbance corrections and add negative absorbance corrections) and use these corrected readings in the calculations if an error, (from this source) of not more than 0.1% can be tolerated.

Cell Corrections (Precise Method)

Fill all four cells with water. Set the absorbance scale at zero with the reference cell in the light path, then read the absorbances of the cells used for the samples. Designate these absorbances as "+" or "−" depending on whether they lie above or below zero. Call this correction factor f_1.

Fill all four cells with a reference solution whose actual absorbance has been determined (either by calculation from the factor, or by measurement using the 0.1 multiplier of the Selector switch). Call this actual absorbance A_r. Set the absorbance scale at zero with the reference cell in the light path, then read the absorbance of the cells used for the samples. Designate these absorbances as "+" or "−" depending on whether they lie above or below zero. Call this correction factor $f_1 + f_2$ (since it includes both cell transparency and path length corrections). Determine f_2 separately by subtracting f_1.

If we now designate the differentially-read absorbance reading of a sample in a particular cell, against the same reference solution (absorbance = A_r), as A_s, the following expression shows how to apply the correction factors to obtain a more precise measure of the true absorbance of the sample solution referred to the reference solution

$$A_s \text{ (corrected)} = \frac{A_r}{A_r + f_2} \qquad [A_s - (f_1 + f_2)]$$

Use this corrected value in the calculations if a more precise result is desired.

Determine the concentration of uranium either by the calibration-curve method or the correction method (20). (*See* "CALCULATIONS"). If the amount of uranium in the sample is not known, make a test run by taking an aliquot of the sample solution and assaying for uranium by the more rapid single extraction method. The standard solutions to be used can then be chosen according to the result obtained.

Table 1

Dilution Table, Regular Method, Solids

Range %	Take gm	Dilute to ml	Take Aliquot ml
1–2.5	1		complete solution
	or 5	25	5
2.5–5.0	0.5		complete solution
	or 5	50	5
5–10	1	25	5
10–20	1	50	5
20–50	1	100	5

Table 2

Dilution Table, Regular Method, Solutions

Range gm/l	Take ml	Dilute to ml	Take Aliquot ml
1–2.5	10	do not	dilute
2.5–5.0	5	do not	dilute
5–10	10	25	5
	or 25	50	5
10–20	5	25	5
	or 10	50	5
20–50	5	50	5
	or 10	100	5

CALCULATIONS

Regular Procedure (250 ml final volume)

Determine absorbance factors (absorbance per mg) for each of the standards carried through the procedure, and if these are reasonably consonant and in agreement with the standard curve, average them. Then

$$\%\ U_3O_8 = \frac{\text{absorbance of sample}}{\text{absorbance factor}} \times \frac{1}{1000} \times \frac{\text{1st dil'n}}{\text{aliq. taken}} \times \frac{100}{\text{sample wt. (gm)}}$$

$$\text{gm/l}\ U_3O_8 = \frac{\text{absorbance of sample}}{\text{absorbance factor}} \times \frac{1}{1000} \times \frac{\text{1st dil'n}}{\text{aliq. taken}} \times \frac{1000}{\text{sample vol.}}$$

$$\left(\text{where } \frac{1}{1000} \text{ is used to convert mg to grams}\right)$$

Example

Three precipitates are to be analysed for uranium by the regular ethyl acetate-colorimetric procedure. U_3O_8 estimations are: sample (a) 15%; sample (b) 40%; sample (c) 70%.

Sample weights —	sample A	5.0 gm
	sample B	3.0 gm
	sample C	2.0 gm

Table 3

Dilutions for Umpire Samples

High Precision (Differential Colorimetric) Method

gm U_3O_8*	Dilute to ml	Take aliquot ml	Gives mg
2.5	200	10	125
3.0	200	10	150
3.5	250	10	140
4.0	250	10	160
4.5	500	15†	135
5.0	500	15†	150
5.5	500	10	110
6.0	500	10	120
6.5	500	10	130
7.0	500	10	140
7.5	550**	10	135
8.0	550**	10	145
8.5	1000	15†	128
9.0	1000	15†	135
9.5	1000	15†	141
10.0	1000	15†	147
10.5	1100**	15†	144
11.0	1100**	15†	150

* Grade, % × weight of sample, grams.

** Available in Giles volumetric flasks.

† Evaporate to approx. 5 ml in a small beaker and wash into separatory funnel.

After dissolution of the sample, all sample solutions are made up to 250 ml. As the aim is to work with 10-30 mg U_3O_8 per 250 ml final volume for colorimetric reading, the aliquots are chosen in the following manner:

SAMPLE A $\frac{12}{100} \times 5000$ mg = 600 mg U_3O_8 in 250 ml, therefore a 10-ml aliquot would contain 24 mg U_3O_8.

SAMPLE B $\frac{40}{100} \times 3000$ mg = 1200 mg U_3O_8 in 250 ml, therefore a 5-ml aliquot would contain 24 mg U_3O_8.

SAMPLE C $\frac{70}{100} \times 2000$ mg = 1400 mg U_3O_8 in 250 ml, therefore a 5-ml aliquot would contain 28 mg U_3O_8.

Three standards are chosen so that 5-ml aliquots contain respectively 20 mg, 25 mg and 30 mg U_3O_8.

If absorbance readings of the three standards are respectively 0.420, 0.528 and 0.626, factors are calculated as follows:

$$\frac{0.420}{20} = 0.0210, \frac{0.528}{25} = 0.0211, \frac{0.626}{30} = 0.0209, \text{ average factor} = 0.0210$$

If absorbance readings of samples A, B and C are respectively 0.480, 0.535 and 0.600, % U_3O_8 in the samples is calculated as follows:

$$\text{(A)}\quad \frac{0.480}{0.0210} \times \frac{100}{5.0} \times \frac{250}{10} \times \frac{1}{1000} = 11.4\%\ U_3O_8$$

$$\text{(B)}\quad \frac{0.535}{0.0210} \times \frac{100}{3.0} \times \frac{250}{5} \times \frac{1}{1000} = 42.5\%\ U_3O_8$$

$$\text{(C)}\quad \frac{0.600}{0.0210} \times \frac{100}{2.0} \times \frac{250}{5} \times \frac{1}{1000} = 71.4\%\ U_3O_8$$

High Precision Procedure (Differential Working)

$$\text{Mg } U_3O_8 \text{ in sample aliquot taken, (C)} = \frac{(C_d - B_d)\,(A - B)}{(A_d - B_d)} + B$$

where A = mg U_3O_8 in highest standard
B = mg U_3O_8 in lowest standard
C = mg U_3O_8 in sample
and
A_d = corrected absorbance of A
B_d = corrected absorbance of B
C_d = corrected absorbance of C

where A is the standard whose absorbance is the closest to that of the sample on its high side and B is the standard whose absorbance is closest to that of the sample on the low side,

then

$$\%\ U_3O_8 = \frac{\text{mg}U_3O_8}{1000} \times \frac{\text{final volume}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt., gm}}$$

$$\text{gm/l } U_3O_8 = \frac{\text{mg } U_3O_8}{1000} \times \frac{\text{final volume}}{\text{aliquot taken}} \times \frac{1000}{\text{sample volume}}$$

Example

A precipitate is to be analyzed for uranium using an ethyl acetate extraction and a colorimetric finish by differential colorimetry. The estimation is 75% U_3O_8 and sample weights (duplicates) D—4.9000 gm D_1—4.6100 gm. After dissolution of the sample, the sample solution is made up to 250 ml and appropriate aliquots chosen as before. The aim is to work between 100-150 mg U_3O_8 per 250 ml final volume for colorimetric reading.

SAMPLE D $\frac{75}{100} \times 4900$ mg = 3675 mg U_3O_8 in 250 ml, therefore a 10-ml aliquot would contain 147 mg U_3O_8

SAMPLE D_1 $\frac{75}{100} \times 4610$ mg = 3458 mg U_3O_8 in 250 ml, therefore a 10-ml aliquot would contain 138 mg U_3O_8.

Four standards are chosen so that 10-ml aliquots contain respectively 110 mg, 130 mg, 140 mg and 150 mg U_3O_8.

Assume that the corrected absorbance readings of samples and standards are as follows:

Standard 110 mg U_3O_8 — this is the base against which all the other absorbances are read.

Standard 130 mg U_3O_8 — 0.256
Standard 140 mg U_3O_8 — 0.380
Standard 150 mg U_3O_8 — 0.502
Sample D — 0.460
Sample D_1 — 0.350

Sample D and D_1 are then calculated as follows: absorbance of sample D (A sample D) falls between absorbances of standards 140 and 150 mg U_3O_8, so % U_3O_8 is calculated

$$\left[\left(\frac{\text{A (sample D)} - \text{A (std 140 mg)}}{\text{A (std 150 mg)} - \text{A (std 140 mg)}} \times 10\right) + 140\right] \times \frac{100}{4.90} \times \frac{250}{10} \times \frac{1}{1000} = \%\ U_3O_8$$

$$\left[\left(\frac{0.080}{0.122} \times 10\right) + 140\right] \times \frac{100}{4.90} \times \frac{250}{10} \times \frac{1}{1000} = 74.77\%\ U_3O_8$$

absorbance of sample D_1 (A sample D_1) falls between absorbances of standards 130 mg and 140 mg U_3O_8, so % U_3O_8 is calculated.

$$\left[\left(\frac{\text{A (sample } D_1\text{)} - \text{A (std 130 mg)}}{\text{A (std 140 mg)} - \text{A (std 130 mg)}} \times 10\right) + 130\right] \times \frac{100}{4.61} \times \frac{250}{10} \times \frac{1}{1000} = \%\ U_3O_8$$

$$\left[\left(\frac{0.094}{0.124} \times 10\right) + 130\right] \times \frac{100}{4.61} \times \frac{250}{10} \times \frac{1}{1000} = 74.61\%\ U_3O_8$$

If, when the colour is developed, it is seen that the samples are below the range assigned to this method, the sample solution (already diluted) together with the relevant information on original sample weight or volume, and dilution, will be transferred to the fluorimetric group and completed by the fluorophotometric method (METHOD U-1).

Where a moisture determination is required, report the result at the same time as the U_3O_8 assay.

Special Instructions Concerning Umpire Analysis

Reporting Results

On umpire samples, the two samples (or aliquots) taken must give results agreeing within 0.6% of the amount present (e.g. 74.8% and 75.3% in this range). If they do not agree within this amount, two more aliquots are carried through the procedure. If three of the four results now agree within 0.8%, they are averaged and reported, for comparison only, with the result from the alternate umpire method (U-5).

If agreement between the two methods is obtained within 0.6% of the average result, it is reported.

If such agreement is not obtained, the sample solution used originally for one method will in each case be analyzed by the other method. If the disagreement is not resolved, the third sample will be weighed, dissolved and aliquotted for determination by both methods in duplicate.

Operating Details

(1) The assay sample must be completely dissolved. (A small amount of white residue is acceptable.)

(2) At least once every two weeks (or once every ten samples, whichever is oftener) check the standard uranium solution used for METHOD U-5. Report the value obtained, and the stated value.

(3) At least once every two weeks (or once every ten samples whichever is oftener) have the standard uranium solutions used in this method checked by METHOD U-5. Report the value obtained and the stated value.

(4) Discard all old standard uranium solutions each month and make up fresh solutions (about a month's supply).

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The Determination of Uranium in Concentrates: Volumetric Cupferron-Titanous Sulphate Reduction Method

METHOD U-5

SCOPE

This is an umpire method, intended principally for the accurate determination of uranium in high-grade ores and products. Routine analysis of high-grade materials should be carried out using the ethyl acetate (1) or thiocyanate colorimetric methods (2).

RANGE

The method has been chosen for samples containing more than 5% U_3O_8.

OUTLINE

The procedure described here is based on the work of Wahlberg et al (3) as modified by Guest (4).

The sample is dissolved, using acids, and taken up to give a solution containing 10% sulphuric acid. The principal elements which interfere in the subsequent titration step (iron and vanadium), are removed by extraction of the cupferrates from the 10% sulphuric acid solution, using chloroform as solvent:

$$6\ C_6H_5N_2OH + Fe_2(SO_4)_3 \longrightarrow 2(C_6H_5N_2O_2)_3\ Fe + 3\ H_2SO_4$$

This step must be carried out at low temperature since cupferron decomposes (to nitrosobenzene) if warm, particularly in the presence of acids. Nitric acid and other oxidizers decompose the reagent and must be absent (5, 6).

The excess cupferron, which interferes in the titration step, is removed, and the uranium is again brought into a sulphuric acid solution. Copper sulphate is added as an indicator and the uranium is reduced with a solution of titanous sulphate in sulphuric acid. The cupric sulphate is reduced after uranium has been completely reduced to the tetravalent state. No reduction of uranium to the trivalent state occurs and any excess of titanous sulphate is used up in conversion of the cupric salt to the metal. Iron, if present, would be reduced before the uranium. It is a peculiarity of the sulphate system that cupric ion is reduced to the metal. (Any cuprous ion formed decomposes to give cupric ion and the metal) (7). It is for this reason that chloride is rigidly excluded from the system since otherwise, the cuprous ion formed would be titrated by the dichromate (8) before the uranium and would be counted as uranium.

$$Ti_2(SO_4)_3 + UO_2SO_4 \longrightarrow 2\ TiO\ SO_4 + U\ (SO_4)_2$$

$$Ti_2(SO_4)_3 + CuSO_4 + 2\ H_2O \longrightarrow Cu + 2\ TiO\ SO_4 + 2\ H_2SO_4$$

The excess of copper metal is dissolved by means of mercuric perchlorate, leaving a clear solution for the titration.

$$2\ Hg(ClO_4)_2 + Cu \longrightarrow Cu(ClO_4)_2 + 2\ Hg\ ClO_4$$

The mercurous perchlorate formed is not oxidized by ferric iron or by dichromate (9).

With the uranium reduced and the excess of copper redissolved and oxidized, an excess of ferric sulphate is added. The uranous ion stoichiometrically reduces ferric iron to ferrous iron.

$$U(SO_4)_2 + Fe_2(SO_4)_3 + 2\ H_2O \longrightarrow UO_2SO_4 + 2\ FeSO_4 + 2\ H_2SO_4$$

This procedure is followed due to the slowness of the direct dichromate-uranous ion titration (10). The ferrous iron formed is then titrated with standard potassium dichromate solution using sodium diphenylamine sulphonate solution as indicator.

$$6\ FeSO_4 + K_2Cr_2O_7 + 7\ H_2SO_4 \longrightarrow 3\ Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + K_2SO_4 + H_2O$$

Phosphoric acid is added to complex ferric iron, reducing its colour (11) and at the same time lowering the oxidation potential of the ferric-ferrous iron system so that the oxidation goes to completion before the indicator is oxidized (12).

The uranium equivalent of the potassium dichromate solution is determined by the titration of a standard uranium solution which is carried through the procedure at the same time as the samples. This is used in place of the normality of the dichromate because it has been found (13, 14) that the uranium equivalent is a function of the volume titrated.

APPARATUS

Mixers, Fisher-Kendall:	
Analytical balance:	
Hot plate, oscillating type:	similar to Fisher 11-492 or Lowe Custom Model (Western Colorado Electric Co.)
Beakers, Pyrex, Griffin low form:	400 ml.
Erlenmeyer flasks, Pyrex narrow-mouth:	500 ml.
Solution evaporators, Fisher-Moroney No-Bump:	Fisher 2-542 400 ml size.
Separatory funnels:	Squibb pear-shaped; 300 ml. (Those with Teflon plugs are preferred.)
Cooling bath:	capable of giving approximately 5°C. One 14" x 28" x 12" deep will provide space for 10 separatory funnels and for the chloroform and cupferron solutions.
Separatory funnel support rack:	
Volumetric flasks, precision recalibrated, with ℸ stoppers:	Kimble 28017, sizes 200, 250 and 500 ml.
Volumetric flask, Giles, with ℸ stoppers:	Kimble 28070, size 500-550 and size 1000-1100.
Pipettes, precision recalibrated:	Kimble 37010, size 10 ml, 15 ml, 20 ml, 25 ml.
Burette, 25 ml:	for adding titanous sulphate.

Graduated cylinders, pharmaceutical: 10 and 25 ml.

Burette, MCA No. 3, Precision Recalibrated: Kimble 17097, 100 ml with 50 ml bulb at top.

Burettes, automatic acid dispensing: 100 ml capacity screw-cap type to fit regular acid winchesters.

Safety glasses:

Rubber gloves:

Tongs, flask:

Tongs, beaker:

Gas burner, Meker type:

REAGENTS

Nitric acid, concentrated: C.P.

Nitric acid, 1:1 (v/v): Add 1 litre of concentrated nitric acid to 1 litre of water in a 4000-ml beaker, stirring constantly.

CAUTION: Wear safety glasses and rubber gloves.

Sulphuric acid, 1:1 (v/v): Prepare in a 4-litre beaker by adding 1 litre of concentrated C.P. sulphuric acid to 1 litre of water in small portions, with constant stirring, cooling as required.

CAUTION: Wear safety glasses and rubber gloves.

When cool dilute to 2 litres with water.

Hydrogen peroxide, 30%: C.P.

Cupferron solution, 8%: Dissolve 40 gm of reagent grade cupferron in distilled water, dilute to 500 ml and filter if necessary. Store in a dark bottle, in a refrigerator, and cool to 5°C before use. The solution should be prepared fresh weekly.

Chloroform, reagent grade: cool to 5°C before use.

Potassium permanganate solution, saturated: about 7% in water.

Potassium permanganate solution, dilute: 1 part saturated solution diluted with 1 part water.

Copper sulphate solution, 5%: Dissolve 25 gm of reagent grade $CuSO_4 . 5 H_2O$ in water and dilute to 500 ml.

Titanous sulphate solution, 10%: Should preferably be made from a starting material containing less than 0.02% iron (on a titanium basis).

Weigh about 5 gm of titanium hydride (Metal Hydrides Inc., Beverly Mass., Grade E) into a dry 50-ml beaker and cover with a dry watch glass. Measure 200 ml of 15% (w/v) sulphuric acid into a 400-ml beaker. At the same time start a supply of about 200 ml distilled water boiling. Bring the acid to a boil on an oscillating hot plate, and add the titanium hydride in 0.5 gm portions over a period of about 1/2 hour.

(NOTE: avoid open flames; hydrogen is given off.) Once every ten minutes or so, remove the beaker from the hot plate, let the gas disengage, and make the solution back up to 200 ml with the boiling distilled water. When the titanium hydride has all been added, and the reaction appears to be over, let the solution cool and decant into a clean bottle. Close with a vented stopper. The solution may be used as long as not more than 10 ml are required to reduce 300 mg U_3O_8. At this point, fresh solution should be prepared.

Titanous sulphate solution (alternative preparations:

(*a*) Place about 5 gm of 99.5% purity titanium metal powder or sponge in about 25 ml of distilled water in a 400-ml beaker and gradually, with heating, enough hydrofluoric acid to bring the metal into solution. Add about 80 ml of 1:1 sulphuric acid and evaporate carefully to low volume, finally taking to heavy sulphuric fumes, using the oscillating hot plate and Moroney evaporator. Dilute the solution to about 200 ml, keeping it 15-20% in sulphuric acid.

(*b*) Dissolve 10 gm reagent grade titanyl sulphate ($TiOSO_4$) in about 50 ml of 1:1 sulphuric acid in a 400-ml beaker, adding 30% hydrogen peroxide in small portions until solution is complete. Dilute to 100 ml, boil, cool and pass through a 1% mercury-zinc Jones reductor column. Adjust the volume to 200 ml and make about 15% in sulphuric acid.

Mercuric perchlorate solution, 8%: Add 25 ml of nitric acid and 10 ml of perchloric acid to 40 gm of mercuric nitrate in a 250-ml beaker. Take to strong fumes of perchloric acid on a hot plate, in a special perchloric acid fume hood. Cool, rinse down the sides of the beaker and once again take to strong perchloric fumes, finally fuming just to dryness. Take up the salt with distilled water and enough perchloric acid to ensure complete solution. Dilute to 500 ml.

Ferric sulphate solution, 20%: Dissolve 200 gm of ferric sulphate with 20 ml of 1:1 (v/v) sulphuric acid and sufficient water to ensure complete solution. Dilute to 1000 ml.

Sulphuric acid-phosphoric acid solution: Mix 74 ml of ortho phosphoric acid (85%) with 26 ml of concentrated sulphuric acid.

Sodium diphenylamine sulphonate solution: Weigh 0.32 gm of barium diphenylamine sulphonate and transfer to a 250-ml beaker containing 90 ml water. Stir while adding 0.5 gm anhydrous sodium sulphate. Let stand 2 hours or more, then filter through a No. 42 Whatman filter paper into a 100-ml volumetric flask, finally diluting to the mark with distilled water.

Standard uranium solution: Put about 13 gm of standard uranium oxide in an accurately tared, wide-mouth drying bottle. Dry in the oven at 105°C for 24 hours, cool in a desiccator, stopper and weigh. Transfer the contents of the weighing bottle completely into a 400-ml beaker, rinsing with 50 ml of 1:1 (v/v) nitric acid. Warm to dissolve. Add 100 ml of 1:1 (v/v) sulphuric acid, place the beaker in a Moroney evaporator on an oscillating hot plate, and evaporate to dense fumes. Cool, cautiously dilute with about 100 ml of water and cool again. Transfer the contents of beaker quantitatively to a 1-litre volumetric flask. Add water to fill the flask to within a few ml of the mark. Mix well, allow to come to standard temperature (20°C) in a thermostatically-controlled water bath, and dilute exactly to the mark with distilled water stored in the bath.

Alternatively, the uranium oxide may be dissolved directly in 1:1 (v/v) sulphuric acid by adding several drops of 30% hydrogen peroxide to the hot solution as needed, taking the solution to fumes to remove the excess hydrogen peroxide.

Standard uranium oxide: MSST (available from the New Brunswick Laboratory), or Temporary Standard No. 1, Port Hope Refinery, Eldorado Mining and Refining Ltd.

Neither of these materials are generally available to the public. If they are unavailable, primary standard potassium dichromate solution may be used without standardizing.

A well-analyzed secondary standard of uranium concentrate similar to that being analyzed may also be set aside and a portion carried through with each batch of samples to check recovery.

Standard potassium dichromate solution (0.025 N): Grind crystalline potassium dichromate (primary standard grade) into a fine powder. Dry in an oven at 150°C. Weigh 1.2259 gm of the dried salt per litre of final volume, and dissolve in distilled water containing 50 ml concentrated sulphuric acid per litre of final volume. Transfer to a volumetric flask of the desired size and make to within a few ml of the mark. Mix well, place the flask in a thermostatically-controlled bath at the standard temperature (20°C) and make to the mark with water adjusted to this temperature. Standardize the solution against the standard uranium solution.

Standardization of Potassium Dichromate Solution

(NOTE: Carry a reagent blank through the procedure described at the end of this section.)

Pipette 15, 20 and 25 ml aliquots of the standard uranium solution (at 20° C, Normax pipettes), (195, 260 and 325 mg U_3O_8) into a 500-ml Erlenmeyer flask. Add 20 ml 1:1 (v/v) sulphuric acid and bring to fumes on the hot plate. Cool, wash down the sides with distilled water and add 15 drops of saturated potassium permanganate solution. Take to fumes again on the hot plate and then fume over a burner until heavy fumes are apparent only at the neck of the flask. Let cool, add 20 ml 1:1 sulphuric acid, and dilute to 40 ml with distilled water. Add a drop or two of 30% hydrogen peroxide and boil to ensure solution. Cool, add 2 ml of 5% copper sulphate solution. Add titanous sulphate solution by means of a 25-ml burette, until a faint permanent darkening of the solution takes place as metallic copper is precipitated. Add an excess of the titanous sulphate solution of about 20% of the initial volume added (e.g. if 5 ml were required, add 1 ml excess). Swirl the solution continually during this step. (If more than 10 ml of titanous sulphate solution is required, this reagent is exhausted and a fresh one should be prepared.) In successive steps, and without undue loss of time, add 10 ml of 8% mercuric perchlorate solution, 15 ml of 20% ferric sulphate solution, and 15 ml of sulphuric-phosphoric solution. After the addition of each reagent, rinse down the sides of the flask and mix thoroughly. Dilute the solution to about 250 ml with distilled water and add 5 drops of diphenylamine sulphonate indicator. Titrate with the standard dichromate solution, taking as the end-point the point when the addition of one drop of dichromate solution causes no further deepening of the violet colour. The titration of a reagent blank, carried through the whole procedure, is subtracted from the titration of the standard.

Procedure for carrying out reagent blank:

Transfer 20 ml of 1:1 sulphuric acid to a 500-ml Erlenmeyer flask, and dilute to 40 ml with distilled water. Add 2 drops of 30% hydrogen peroxide (enough to reduce all the titanous sulphate to be added except about 1 ml), but do not boil. Add 2 ml of 5% copper sulphate solution. Add the same volume of titanous sulphate as was used, on the average, for the samples (including the excess). Swirl the solution continually during this step. Continue the balance of the procedure in exactly the same manner as for the samples and subtract the titration so obtained from the titration of the samples.

The uranium factor of the dichromate solution is given by:

$$\text{factor (ml 0.025N } K_2Cr_2O_7 \text{ solution per mg } U_3O_8) = \frac{\text{Titration of standard} - \text{blank titration}}{\text{mg } U_3O_8 \text{ in aliquot taken}}$$

PROCEDURE

1. Pre-Analysis Treatment—for samples other than Port Hope Umpire Samples

(a) Preliminary Examination

Examine the sample carefully to ensure that it has been properly ground. Any samples that appear to have an appreciable quantity of + 100 mesh material must be returned to the sample preparation section for pulverizing. Note also if foreign materials appear to be present.

(b) Rolling: Kendall Mixer Method

Roll the sample for 30 minutes on the Kendall mixer, removing and shaking two or three times during this interval. Use a bottle that is not more than half full (preferably 7-8 ounces of sample in a 16-ounce bottle). If the sample bottle is too full for proper agitation, transfer the complete contents to a properly labelled dry bottle of the right size, and seal tightly.

2. Sample Solution

(a) Port Hope Umpire Samples

Assay samples of about 10 gm each are prepared at Port Hope and supplied in three plastic, stoppered vials, the whole top of which is sealed with sealing wax. Take one vial only for the determination by this method.

Immediately prior to weighing the sample, remove the sealing wax carefully and completely with a knife, without disturbing the stopper. Remove all loose particles, wipe well with a chamois and carefully weigh the whole vial including cap and contents on an accurate analytical balance. Remove the cap gently, and carefully transfer the sample to a 400-ml beaker, avoiding dusting and the transfer of any loose particles of sealing wax.

Reweigh the cap and vial immediately, avoiding unnecessary handling. (Note that it is not necessary to transfer any small amount of sample adhering to the vial.) The difference in weight between the full and empty vial is the true weight of sample taken.

Carefully wet the sample with water and add 60 ml 1:1 nitric acid. Boil for 5 minutes. Cool, wash down the sides of the beaker and add 50 ml of 1:1 sulphuric acid. Place the beaker in a Moroney evaporator and take to fumes on an oscillating hot plate. Cool, cautiously add about 100 ml of distilled water with constant swirling, and warm till all soluble salts are in solution. If the material is difficultly soluble, add a few drops of 30% hydrogen peroxide to hasten solution. Transfer to a volumetric flask of suitable size, according to the grade of the material (*see* Table 1), add sufficient 1:1 sulphuric acid to give 5% in the final volume and make to the mark at 20° C.

(b) Other Chemical Concentrates

Measure out one or two samples rapidly into tared, 12-ml, glass-stoppered weighing bottles which have been allowed to come to equilibrium in the balance case. Do not take the time to weigh out a stated amount, but measure out the required amount approximately, using a suitable measuring spoon. At the same time, measure out samples for the other umpire uranium method (Differential Colorimetric Modification, METHOD U-4), as well as the sample for moisture determination (Oven Method Modification, METHOD M-1). Immediately stopper both the sample bottle and weighing bottles and weigh the weighing bottles exactly, determining the sample weight taken by difference. Choose a sample size ($\simeq$ 10 gm) sufficient to provide a representative portion of the whole sample. Transfer to a 400-ml beaker, rinsing the bottle with water and then with 60 ml of

1:1 nitric acid. Continue the balance of the preparation as outlined in Section 2(a), fourth para. (for Port Hope Umpire Samples), and choose dilutions and aliquots so that the final aliquot taken for titration will contain 280-350 mg U_3O_8.

(*c*) *Ore Samples*

Weigh out the samples as in above para. Transfer the contents of the weighing bottle to a 250-ml beaker and rinse the bottle with 15 ml of hydrochloric acid. Cover the beaker and boil for 10 minutes. Cool, wash down the sides of the beaker and add 15 ml of nitric acid, 1 ml of 40% hydrofluoric acid and 15-20 ml of 1:1 sulphuric acid. Place the beaker in a Moroney evaporator and take to sulphuric fumes once on the oscillating hot plate. Continue as in Section 2(a) fourth para., (Port Hope Umpire Samples), choosing dilutions and aliquots so that the final aliquot contains 280-350 mg U_3O_8.

3. Cupferron Extraction

Pipette duplicate aliquot portions containing 280-350 mg U_3O_8 (*see* Table 1) into a 300-ml separatory funnel. At the same time pipette 25-ml aliquots of the standard uranium solution into similar funnels. Add sufficient 1:1 sulphuric acid to give a total content equivalent to 10 ml of the concentrated acid. Dilute to 100 ml, add dilute potassium permanganate until the sample is just pink, and cool to 5° C.

Add 30 ml of 8% cupferron solution (cooled to 5° C) and shake. Extract with one 40-ml and two 30-ml portions of cold chloroform, or until the chloroform layer is clear after shaking. Add another 30 ml of 8% cupferron, shake, and again extract with chloroform. If the precipitate that appears upon addition of the cupferron is white, the separation is complete. Otherwise the extraction step must be repeated until no change is noticed in the colour of the precipitate upon successive additions of cupferron.

After completion of the final chloroform extraction, wash the sample solution into a 500-ml Erlenmeyer flask. Add one glass bead and evaporate the solution to about 35 ml on an oscillating hot plate.

Add 35 ml of nitric acid and bring to fumes of sulphuric acid on the hot plate. Cool, wash down the sides of the flask with distilled water and add 15 drops of saturated potassium permanganate solution. Take to fumes again, finally fuming over a Meker burner until heavy fumes are apparent only at the neck of the flask. The steps of this paragraph must be repeated until all organic matter is removed.

4. Reduction and Titration

(NOTE: Carry a reagent blank as described at the end of this section.)

After the solution has cooled, adjust the acidity so that about 20 ml of 1:1 sulphuric acid is present. Dilute the solution to 40 ml with distilled water and add a drop or two of 30% hydrogen peroxide. Boil to dissolve completely. Cool and add 2 ml of 5% copper sulphate solution. Add titanous sulphate solution by means of a 25-ml burette, until a faint permanent darkening of the solution takes place as metallic copper is precipitated. Add an excess of the titanous sulphate solution of about 20% of the initial volume added (e.g. if 5 ml were required, add 1 ml excess). Swirl the solution continuously during this step. (If more than 10 ml of the titanous sulphate solution is required, this solution is exhausted and a fresh one should be prepared.)

In successive steps, and without undue loss of time, add 10 ml of 8% mercuric perchlorate solution, 15 ml of 20% ferric sulphate solution, and 15 ml of sulphuric-phosphoric solution. After the addition of each reagent, rinse down the sides of the flask and mix thoroughly. Dilute the solution to about 250 ml and add 5 drops of diphenylamine sulphonate indicator. Titrate with the standard dichromate solution, taking as the end-point, the point when the addition of one drop of dichromate solution causes no further deepening of the violet colour. The titration of a reagent blank, carried through the reduction and titration step, is subtracted from the titrations of samples and standards.

Procedure for Carrying out Reagent Blank:

Transfer 20 ml 1:1 sulphuric acid to a 500-ml Erlenmeyer flask, and dilute to 40 ml with distilled water. Add 2 drops of 30% hydrogen peroxide (enough to reduce all the titanous sulphate added except about 1 ml), but do not boil. Add 2 ml of 5% copper sulphate solution. Add the same volume of titanous sulphate as was used, on the average, for the samples (including the excess). Swirl the solution continually during this step. Continue the balance of the procedure in exactly the same manner as for the samples and subtract the titration so obtained from the titration of the samples.

CALCULATIONS

$$\% \ U_3O_8 = \frac{(\text{ml dichromate, sample titration} - \text{blank})}{\text{factor} \times 1000} \times \frac{100}{\text{sample wt. gm}} \times \frac{\text{dil.}}{\text{aliq. taken}}$$

where the factor is given by:

$$\text{ml } K_2Cr_2O_7/\text{mg } U_3O_8 = \frac{\text{ml dichromate, standard titration} - \text{blank}}{\text{mg } U_3O_8 \text{ in standard}}$$

Where a moisture determination is required, report the result at the same time as the U_3O_8 assay.

Special Instructions Concerning Umpire Analysis

Reporting Results

On umpire samples, the two aliquots titrated must agree within 0.6% of the amount present (e.g. 74.8% and 75.3%, in this range). If they do not agree within this amount, two more aliquots are carried through the cupferron and titration steps. If three of the four results now agree within 0.8%, they are averaged and reported for comparison only with the result obtained using the differential colorimetric modification of METHOD U-4.

If agreement between the two methods is obtained within 0.6% of the average result, the average result is reported. If such agreement is not obtained, the sample solution used originally for one method will in each case be analyzed by the other method. If the disagreement is not resolved, the third sample will be weighed, dissolved and aliquotted for determination by both methods in duplicate.

Operating Details

1. The assay sample must be completely dissolved. (A small amount of white residue is acceptable.)

2. At least once every two weeks (or once every 10 samples, whichever is oftener) check all the standard uranium solutions used for METHOD U-4 by METHOD U-5. Report the value obtained, and the stated value.

3. At least once every two weeks (or once every 10 samples, whichever is oftener) have the standard uranium solution used in this method checked by METHOD U-4. Report the value obtained, and the stated value.

4. Discard all old standard uranium solutions each month, and make up fresh solutions.

Table 1

Dilution for Umpire Samples

gm U_3O_8*	Dilute to, ml	Take ml	Gives, mg U_3O_8
2.5	250	25	250
3.0	250	25	300
3.5	250	20	280
4.0	200	15	300
4.5	200	15	340
5.0	250	15	300
5.5	250	15	330
6.0	200	10	300
6.5	200	10	325
7.0	200	10	350
7.5	500	20	300
8.0	500	20	320
8.5	500	20	340
9.0	550**	20	327
9.5	550**	20	345
10.0	500	15	300
10.5	500	15	315
11.0	500	15	330

* Estimated U_3O_8 assay × weight of sample

** Available in Giles volumetric flask

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The Determination of Uranium: Rapid Colorimetric Thiocyanate Method Using Cupferron-Hydrochloric Acid Separation

METHOD U-6

SCOPE

This method is intended as an alternative to METHOD U-3. It is somewhat more convenient to use and is particularly useful for samples high in thorium.

RANGE

The range is 0.005 to 1.0% or gm/l using 1-cm cells. The 95% confidence interval for 2 mg U_3O_8 (0.100% U_3O_8, 2-gm sample) is $\pm$ 0.6% of the amount present (i.e. 0.994 to 0.106%).

OUTLINE

The principal cations that interfere in the colorimetric thiocyanate method for uranium are molybdenum, vanadium, titanium(1), cobalt, lead, chromium, nickel and possibly bismuth (2)(3). Iron above 0.2 gm/l in the final solution for colour development causes high results, and while this can be overcome by increasing the amount of stannous chloride used for reduction, there eventually comes a point where this is no longer effective. Copper gives a white precipitate if more than 1 gm/l is in the final solution, and more than 10 gm/l of thorium depresses the colour. Zirconium also interferes slightly (3).

Cobalt, lead, nickel and chromium are not removed by the cupferron treatment. The interference of the first two is the most serious but can be eliminated (with some loss in sensitivity for uranium however) by measuring the absorbance at 400 mμ instead of at 370 mμ.

Chromium is volatilized as chromyl chloride in the procedure given(5). Nickel will have to be removed by a carrier-precipitation of uranium using carbonate-free ammonia if it is present in concentrations exceeding that of the uranium, but this does not form part of the method outlined here.

The only anion commonly found in the solutions from ores and process solutions (other than sulphate) which interferes with the development of the uranyl thiocyanate colour is fluosilicate, which at a concentration of 0.1 gm/l in the final volume causes a 10% reduction in the colour(3). Its presence is avoided by the fuming step using perchloric acid, which volatizes fluosilicic acid.

The thiocyanate colour is normally developed in a hydrochloric acid medium due to the depressing effect of the sulphate ion. An extremely convenient way of eliminating most of the above interferences from a hydrochloric acid solution is by extraction of the cupferrates. Uranyl ion is not extracted at all. Titanium,

molybdenum, vanadium(1), zirconium, copper, stannic tin and ferric iron are completely extracted. Thorium and ceric cerium are almost completely extracted, and bismuth, tungsten and antimony are partly extracted(4, 5).

APPARATUS

Beakers, Griffin, low-form:	250 ml size
Funnels, separatory, with Teflon stopcock plugs:	125 ml size
Pipettes:	1, 2, 5, 25 and 50 ml sizes
Graduates, pharmaceutical:	10, 35 and 60 ml
Rack for separatory funnels:	
Spectrophotometer, Beckman Model DU:	
Spectrophotometer cells, Corex:	1 cm and 5 cm

REAGENTS

Hydrochloric acid, concentrated C.P.:	
Hydrochloric acid, 10% v/v:	
Nitric acid, concentrated:	
Perchloric acid, concentrated:	
Potassium permanganate solution, saturated:	about 7% in water. Store in a dropping bottle.
Cupferron solution, 8%:	Dissolve 8 gm cupferron in 100 cc of water and filter if necessary. Make up fresh as needed and keep at 5°C. It can be kept somewhat longer if stored in a dark bottle.
Chloroform, reagent grade:	Cool to 5°C if possible.
Stannous chloride, 10%:	Dissolve 10 gm of stannous chloride in 10 ml of concentrated hydrochloric acid by warming on a hot plate. Cool and dilute to 10 ml with distilled water. Make up fresh daily.
Ammonium thiocyanate solution, 50%:	Dissolve 50 gm ammonium thiocyanate in distilled water, filter and adjust the volume to 100 ml. Make the solution up fresh daily or store in a dark bottle.
Standard uranium solution:	Dissolve 0.500 gm of 99.9% U_3O_8 by means of hydrochloric and nitric acids, and take to dryness. Take up in 25 ml of 1:1 hydrochloric acid, transfer to a 2-litre volumetric flask and make to volume using 10% hydrochloric acid:—1 ml = 0.25 mg U_3O_8.

Preparation of Standard Spectrophotometric Calibration Curve

Transfer aliquots of the standard solution containing 1.0, 2.0, 5.0, 10.0, and 25.0 ml (for the curve using 1-cm cells), and 0.5, 1, 2, 3 and 5 ml (for the curve using 5-cm cells), to 100-ml volumetric flasks. Make to about 50 ml with 10% hydrochloric acid, add 2 ml of 10% stannous chloride and swirl to mix. Add 25 ml of 50% ammonium thiocyanate, swirl, make to volume with distilled water and mix well. Determine the optical density at 370 mμ and at 400 mμ, and make up separate curves of optical density vs. uranium content for each cell path length and wave length.

PROCEDURE

Sample Preparation

Solid Samples

Weigh a 1 - to 10-gm sample of the ore into a 250-ml beaker. Moisten with water, add 20 ml of hydrochloric acid, cover and digest on a hot plate for 10 minutes. Add 10 ml of nitric acid, cover and digest 5 minutes more. Evaporate to near dryness. Cool, add 5 ml of nitric acid, 15 ml of perchloric acid and bring to fumes of perchloric acid.

If chromium may be present add 1 gm of sodium chloride and fuse until chloride is eliminated. Bring to fumes again and repeat twice with 0.5-gm portions of sodium chloride, maintaining about 15 ml of perchloric acid.

In either case fume to dryness. Cool, and leach the residue with several 10-ml portions of 1:1 hydrochloric acid by digesting on a steam bath. Filter into a 150-ml beaker and evaporate to about 5 ml. Make to about 25 ml with water.

Solution Samples

Pipette a suitable aliquot directly into the separatory funnel, if chromium and fluoride are known to be absent. Otherwise pipette the aliquot into a 250-ml beaker, evaporate to dryness and proceed as for solid samples.

Cupferron Extraction

Transfer the sample solution to a 125-ml separatory funnel, washing the beaker with water, and adjust the volume to about 50 ml with water. In the case of solution samples pipette a suitable aliquot (1-10 ml) directly into the funnel and add sufficient 10% hydrochloric acid to give a total volume of about 50 ml.

Mix well and add sufficient saturated potassium permanganate solution (dropwise with shaking) to impart a permanent pink colour to the solution. Cool the separatory funnel (the cooler the better but in any case below room temperature), and add 15 ml of cold 8% cupferron solution. Mix well, add 15 m of chloroform and shake for 10 seconds. Let the layers separate, drain and discard the organic layer. Repeat the addition of chloroform and the extraction step three more times. (Traces of cupferron interfere in the colorimetric finish.) Pour the aqueous layer from the top of the separatory funnel (not through the stem) into a 100-ml volumetric flask. Rinse the funnel with water (5-10 ml) and add to the flask.

Colour Development

To the volumetric flask, add 2 ml of 10% stannous chloride, stopper and shake well. Add 25 ml of 50% ammonium thiocyanate, mix well, make to volume with distilled water and mix again. Determine the optical density of the solutions on the Beckman DU spectrophotometer at 370 mμ (400 mμ if cobalt or lead are present), using 1-cm or 5-cm Corex cells. Record the optical density and determine the uranium content of the final solution by means of a graph of uranium concentration vs. optical density for the particular cell path and wave length used.

CALCULATIONS

Solids

$$\% \ U_3O_8 = \frac{\text{mg } U_3O_8 \text{ (from graph)}}{1000} \times \frac{100}{\text{sample wt.}}$$

Solutions

$$\text{gm/l } U_3O_8 = \frac{\text{mg } U_3O_8 \text{ (from graph)}}{1000} \times \frac{1000}{\text{sample vol. taken}}$$

If the sample gives the same reading as the blank, report the uranium content as "less than" the minimum amount detectable. This corresponds to 0.1 mg of U_3O_8, using 5-cm cells, wave length 370 mμ (optical density $\doteq$ 0.100), and the figure to report would be e.g. 0.005% for a 2 gm-sample.

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The Determination of Thorium Gravimetrically and Colorimetrically Following Sebacic Acid and Mesityl Oxide Separations

METHOD Th-1

1. SCOPE

The method outlines a number of procedures for the analysis of all types of thorium-bearing materials, based on the use of sebacic acid precipitation and solvent extraction with mesityl oxide as preliminary purification steps. Provision for determining the thorium content (*of ore samples only*) radiometrically using the thorium emanation method, on the same solution which is subsequently treated by this method, is also described. Details of a colorimetric finish for the lower concentrations and a gravimetric finish for the higher concentration range are provided.

2. RANGE

The lower limit of the method using the colorimetric modification is 0.005% or 0.005 gm/l ThO_2 if zirconium, titanium, niobium and tantalum are not present in large amounts. With material in which these constituents predominate, the lower limit is 0.05%. The colorimetric finish can be used for up to 50% ThO_2, but for the range 25% ThO_2 and up the gravimetric procedure is preferable.

3. OUTLINE

Properties of Thorin Reagent

Thorium, at low concentrations in acid solutions, reacts with the orange-coloured compound "Thorin", (2-(2 hydroxy-3, 6 disulpho-1 naphthyl azo)-benzene arsonic acid) to give a red colour which is suitable for spectrophotometric analysis over a fairly wide range (1, 2, 3). The coloured complex contains one atom of thorium and two molecules of "Thorin" and at high concentrations tends to precipitate. It is stable for over a month at room temperature, but may decompose if kept above 35° C. The reagent solution is also very stable. The optimum pH for colour development is in the range 0.5 to 1.5, and the developed colour shows a slight positive temperature coefficient (4).

Of the elements commonly found in Canadian ores, titanium and zirconium present the most serious interferences, both giving red precipitates with the reagent at low concentrations.

The uranyl ion (UO_2^{++}) causes only slight interference, 5 mg of uranium in 100 ml being equivalent to about 20γ of thorium. Uranous uranium is a very serious interference and must be absent.

Both ferric and ferrous iron interfere, the former giving a serious non-linear interference. The use of a suitable reducing agent (i.e. one that will reduce iron without reducing uranium, such as hydroxylamine), will reduce the interference of small amounts of iron, but it should preferably be removed. Aluminum is a much less serious interference (10 mg are approximately equivalent to 6γ ThO_2) and it has in fact been proposed to add aluminum to overcome the interference of fluoride.

The rare earths interfere in two ways—(1) by producing a colour with the reagent, and (2) in larger amounts by reducing the effective concentration of the reagent and causing a diminution in colour. The net result of this is that if a calibration graph is constructed using varying amounts of thorium, but in each case a constant amount of the rare earth, there will be a positive intercept at zero thorium content and the slope of the curve will be reduced. Read alone,

the rare earths do not give a straight line graph. Ce^{III}, La, Sm and Y, (in decreasing order of importance) are the principal interfering rare earths insofar as complexing the reagent is concerned. As for colour development, 5 mg Ce^{III} is equivalent to 11 γ ThO_2, 5 mg Y to 40 γ ThO_2, and Nd gives no colour at least up to 60 mg per 100 ml volume. Ce^{IV} bleaches the colour and must be absent. (Its effect can be removed by hydroxylamine hydrochloride in the same way as for iron.) With this exception, up to about 5 mg rare earths can be tolerated in all but the most careful work (16).

The alkalis, alkaline earths and ammonia interfere by causing colour diminution. Lithium is the most and sodium and ammonium the least serious of these. Barium does not interfere up to 200 mg per 100 ml volume, but above this concentration gives a precipitate.

Tin is a serious interference in both valence states and must be absent. Lead chloride precipitates in the chloride medium used for colour development, but can be tolerated up to 125 mg per 100 ml.

Of the anions, only chloride and nitrate can be tolerated. Fluoride and phosphate interfere very seriously, and sulphate, though not as serious, must also be absent. Nitrate has a slight effect, 1.5 gm reducing the absorbance by about 1%. Chloride is substantially without effect. Organic acids, sulphite and thiosulphate, and carbonates interfere and must be absent (1, 5).

Fluoride Separation

Many of these interferences are eliminated in the preliminary treatment of the sample (by fusion with anhydrous potassium fluoride and the subsequent solution in hydrofluoric acid, or by hydrofluoric acid treatment alone. Centrifugation of the precipitated fluorides, followed by decantation and washing, eliminates the bulk of the titanium, zirconium, niobium, tantalum, iron, aluminum, and beryllium, all of whose fluorides are soluble in hydrofluoric acid. Uranium IV, the alkaline earths, the rare earths, lead and indium remain with the thorium (6, 7).

Thorium fluoride is highly insoluble, but difficult to filter. Centrifugation of small amounts tends to result in losses, but the use of lanthanum fluoride as a collector overcomes this and permits quantitive recovery of as little as 50 γ ThO_2 (8). Indeed, recovery of less than 1 γ has been reported in the literature (9).

The formation of thorium oxyfluoride (which is difficult to redissolve) in the potassium fluoride fusion, can be reduced by protecting the melt from the atmosphere using CO_2 formed by the oxidation of a layer of sugar charcoal on top and by not prolonging the fusion unnecessarily.

Thorium Emanation, Radiometric Method

In the case of ores *only*, after the initial attack, (complete solution is required and no separations are permissible), thorium is determined by the emanation method. This method (10) is rapid and accurate and can be used alone if desired. It is based on the detection of alpha particles in a gas or air stream which passes through the thorium-containing solution. The particles, which are detected by a scintillation counter, are derived from thoron, half-life 54.5 seconds; thorium A, half-life 0.16 seconds; thorium C^{I}, half-life 0.3 micro-seconds; and thorium C^{II}, half-life 3.1 minutes. Thoron and thorium A contribute at least 98% of the particles.

Radon, the corresponding gaseous member of the uranium series, has a much longer half-life than thoron (3.82 days) and therefore little of it decays in the time taken for the gas to pass through the scintillation chamber. Once the accumulated radon has been eliminated by boiling, followed by further de-emanation just before counting, its rate of growth and decay are such that it does not interfere even when the uranium: thorium ratio is as high as 100 to 1.

Using the instrument at the Mines Branch the standard deviation on the standard solution, (approx. 20 mg ThO_2 per 200 ml of solution) amounts to ± 1.73%, expressed as a percentage of the mean at this concentration level.

Sebacic Acid Separation

Following elimination of the fluoride, using nitric and perchloric acids (or on the solution from the thorium determination by the emanation method) a sebacic acid separation is carried out at pH 2.6 to 2.8, in the presence of oxalate and hydroxylamine. Oxalate complexes a number of ions such as titanium, zirconium and bismuth which would otherwise tend to hydrolyze and precipitate at this pH. It is added as methyl oxalate to suppress the tendency for rare earth oxalates to precipitate until the sebacate complexes are well established. Co-precipitation of rare earths, (particularly cerium and the lanthanum carrier) and of calcium is nevertheless high (8).

Hydroxylamine addition serves both to reduce ceric and ferric ions and to complex uranium (11). Other ions are apparently held in solution as soluble sebacates (12, 13, 14). Once again, lanthanum is added, partly as a carrier, and partly because it seems to displace some thorium which would otherwise not be precipitated.

Sulphate interferes seriously and must be absent. This is usually accomplished by means of an ammonia precipitation, with or without sebacic acid. This step also removes calcium.

The overall separation, while not clear-cut, has been shown experimentally (8) to reduce the concentration of many interfering ions, particularly zirconium, iron and uranium, to levels which can be tolerated in the colorimetric finish. One disadvantage of the step is that recovery occasionally has a tendency to be low.

Mesityl Oxide Separation

The fluoride precipitate, (or if the sebacic acid separation was used, the redissolved sebacate precipitate) is taken up in nitric acid and aluminum nitrate salting solution, the aluminum complexing the fluoride to give a clear solution. The thorium is then quantitatively extracted with mesityl oxide, $(CH_3)_2 C{:}CHCOCH_3$, (an unsaturated aliphatic ketone) containing 5% hexane. The hexane addition improves the phase separation and reduces the tendency of mesityl oxide to darken or char. Charred mesityl oxide gives inefficient thorium extraction. Excessive amounts of hexane also reduce the extraction efficiency, however. Charring is also reduced by cooling the solutions used for extraction and by using minimum contact time between the acid aqueous solutions and the solvent.

The aluminum nitrate salting agent serves most of the functions that it does in the ethyl acetate extraction as described in METHOD U-4, and the theoretical considerations governing the extraction are similar.

This separation eliminates the alkalis, alkaline earths, most of the rare earths, (including Ce^{IV} which is apparently reduced to Ce^{III} by the mesityl oxide and is therefore not extracted), lead, and indium. Small amounts of aluminum, iron, yttrium and vanadium are extracted. Uranium (VI) (and any zirconium not eliminated in the fluoride treatment) will accompany the thorium (15).

Treatment of Hydrofluoric Acid Burns

Instantly flush the affected part in running water. Always keep a large beaker of a saturated solution of borax in a convenient place and use to rinse the hands at regular intervals. Apply to burns after thoroughly rinsing the part with water.

Always wear safety glasses and wear rubber gloves whenever convenient. Do *not* wear gloves if conditions are such that they will increase the possibility of spilling or dropping the acid.

For extensive burns, have someone seek medical aid *at once*, but remain and continue flushing the part with water from the safety showers till aid arrives.

4. APPARATUS

Dishes, platinum:	60 ml and 150 ml sizes.
Crucibles, platinum:	30 ml size.
Stirring rod:	cut from $\frac{1}{8}$" nickel welding rod.
Beakers, Pyrex, Griffin low form:	250, 400 and 600 ml sizes.
Funnels, filtering, Bunsen long stem:	
Filter papers, Whatman No. 41 H:	
No. 42:	7, 9 and 12 cm sizes.
No. 50:	
Asbestos paper:	7/16" thick, perforated with 1" holes on 2-inch centres. Use to pad portions of the hot plate in single and double thicknesses to provide various temperatures for evaporations, to prevent warping the plate.
Funnels, separatory, Squibb:	60 ml and 125 ml sizes.
Stoppers, polyethylene:	Fisher 14-645.
Pipettes, volumetric:	5, 10, 25, 50 ml sizes.
Flasks, volumetric:	25, 100, 250, 500 ml sizes.
Centrifuge, International Type C:	
Bottles, centrifuge, high temperature polyethylene:	250 ml size (8 oz.) e.g. Scientific Glass Cat. No. C-3355X.
Steam bath:	
Hot plate:	padded with 1 and 2 thicknesses of perforated 1/16" asbestos paper.
Infra red lamps:	
Propane gas:	to supply blast burner.
Compressed air:	
Filtering apparatus, vacuum:	similar to Fisher Filtrator, Fisher Cat. No. 9-788.
Blast burner:	similar to Fisher Cat. No. 3-910-5.
Safety glasses:	
Rubber gloves:	
Thorium emanation apparatus:	*See* Figures 1A, 1B, 2, 3, 4, 5 and 6.

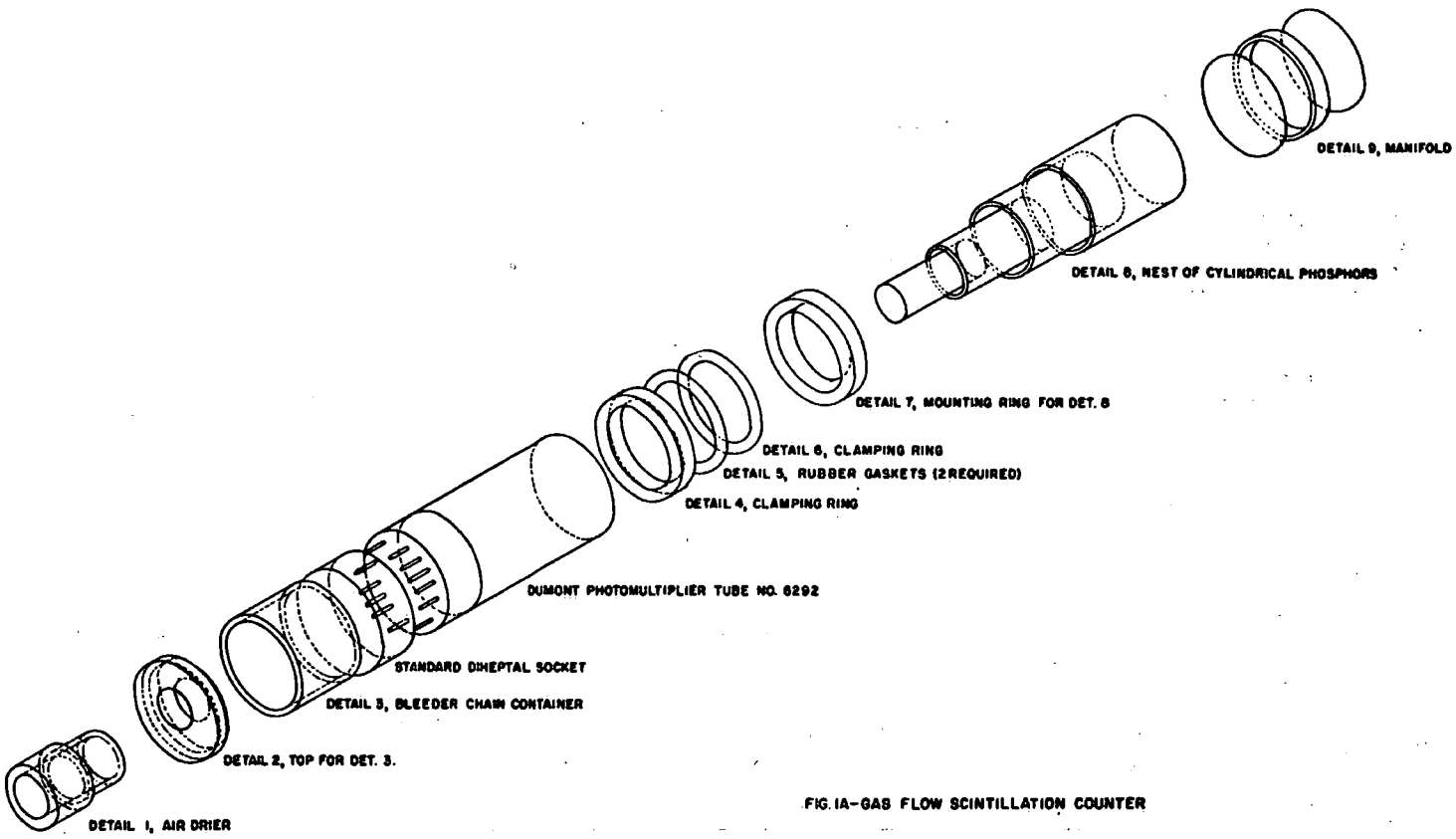
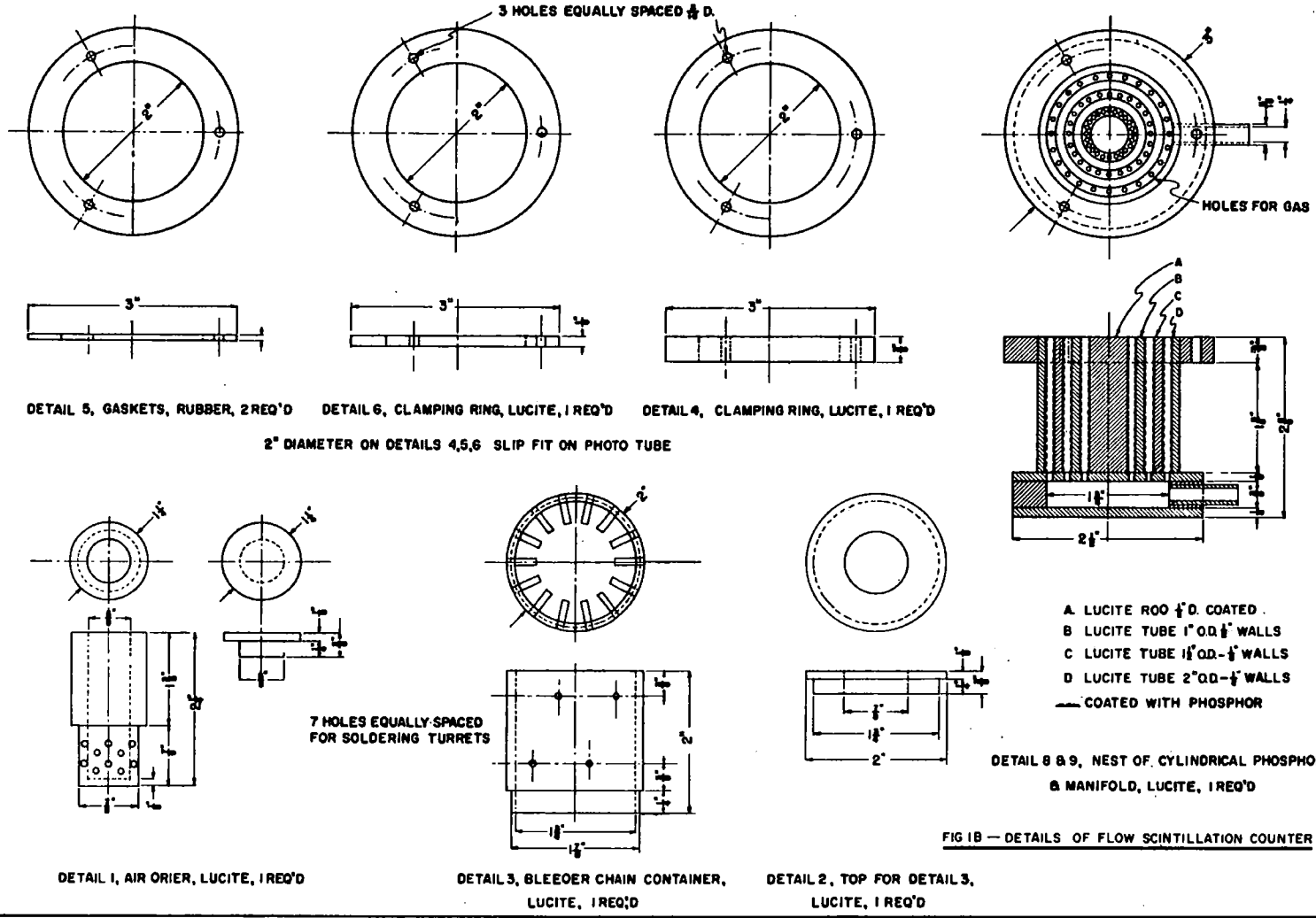


FIG. IA–GAS FLOW SCINTILLATION COUNTER



DETAIL 5, GASKETS, RUBBER, 2 REQ'D

DETAIL 6, CLAMPING RING, LUCITE, 1 REQ'D

DETAIL 4, CLAMPING RING, LUCITE, 1 REQ'D

2" DIAMETER ON DETAILS 4,5,6 SLIP FIT ON PHOTO TUBE

DETAIL 8 & 9, NEST OF CYLINDRICAL PHOSPHORS & MANIFOLD, LUCITE, 1 REQ'D

DETAIL 1, AIR ORIER, LUCITE, 1 REQ'D

DETAIL 3, BLEEDER CHAIN CONTAINER, LUCITE, 1 REQ'D

DETAIL 2, TOP FOR DETAIL 3, LUCITE, 1 REQ'D

FIG 1B — DETAILS OF FLOW SCINTILLATION COUNTER

A zinc sulphide phosphor and Dumont type 6292 photomultiplier tube combination (Figures 1A and 1B) is used for alpha detection. The scintillation chamber is composed of a nest of concentric Lucite cylinders 2″ long, $\frac{1}{8}$″ thick and 2″, $1\frac{1}{2}$″ and 1″ in diameter, the centre being occupied by a $\frac{1}{2}$″ × 2″ Lucite rod. All surfaces of the Lucite pieces except the outside surface of the 2″ cylinder are coated with silver-activated zinc sulphide powder.

The zinc sulphide coating (New Jersey Zinc Co., zinc sulphide No. 2330) is applied by first painting the Lucite surfaces with a thin mixture of Glyptal cement and acetone, then dusting the zinc sulphide on the coated surface through a piece of clean cloth.

The coated cylinders are mounted on a Lucite manifold $\frac{5}{8}$″ thick and $2\frac{1}{2}$″ in diameter in such a manner that gas flowing through three rows of small perforations in the top of the manifold, rises between the walls of the concentric coated cylinders (detail Figure 1B). This arrangement has the advantages of (a) good geometry, as the chance of an alpha particle striking the phosphor is high because of the small distance between adjacent cylinder walls, (b) the close proximity of the cylinder walls lessens the effect of turbulence within the rising gas, (c) a large area of phosphor is exposed to possible alpha radiation, and (d) as all the walls are covered by phosphor material, there is no loss of scintillations due to the absorbance of thoron on the scintillator walls.

The phosphor assembly is attached to a Dumont 6292 photomultiplier tube by means of a Lucite yoke so that a small space is left between the phosphor and the window of the tube for the free escape of the partially-spent activating gas. The Lucite yoke comprises two Lucite rings with a piece of soft rubber between (Figure 1A). Tightening the bolts of the yoke squeezes the rubber slightly from between the rings, holding the yoke firmly on the photomultiplier tube.

The voltage-dividing chain for the photomultiplier tube is contained in a cylindrical Lucite container firmly attached to the base of the tube socket. Inserted through the top of the Lucite cylinder is a removable container designed to expose a drying agent such as silica gel to the voltage-dividing network.

The thorium sample in acid solution is placed in a cylindrical, glass, sample holder (Figure 2) closed at the bottom and top with rubber stoppers. A fritted-glass filter tube passes through the bottom stopper and allows air under pressure to be diffused through the sample in small bubbles. The top stopper has a piece of glass tubing passing through it, which allows the thoron-enriched gas or air to pass first through a water-cooled condenser, then to the alpha detecting combination (Figure 4).

The sample holder is easily filled or emptied of sample solution, and rinsed clean, by disengaging it from the supporting clips and removing one or both stoppers.

A slight flow of air is required when filling the sample holder to prevent a portion of the sample solution from backing up through the fritted-glass diffuser.

Air for entraining the thoron is fed to the sample holder from a gasometer constructed from two 13-gallon polyethylene carboys as shown in Figure 3.

This arrangement gives a head of pressure which is sufficiently constant for a thorium determination.

The bottom carboy is filled with water; then air from a compressed air line or portable pump is forced into it, raising the water through the siphon to the top carboy. When nearly all the water is raised, with sufficient left to cover the bottom end of the siphon, the air is turned off. Opening a valve on the top of the bottom carboy allows air under pressure from the head of water in the siphon to flow first through a modified Venturi flow-meter (5), then through the sample solution.

One filling of the top carboy is sufficient to run the apparatus for one day.

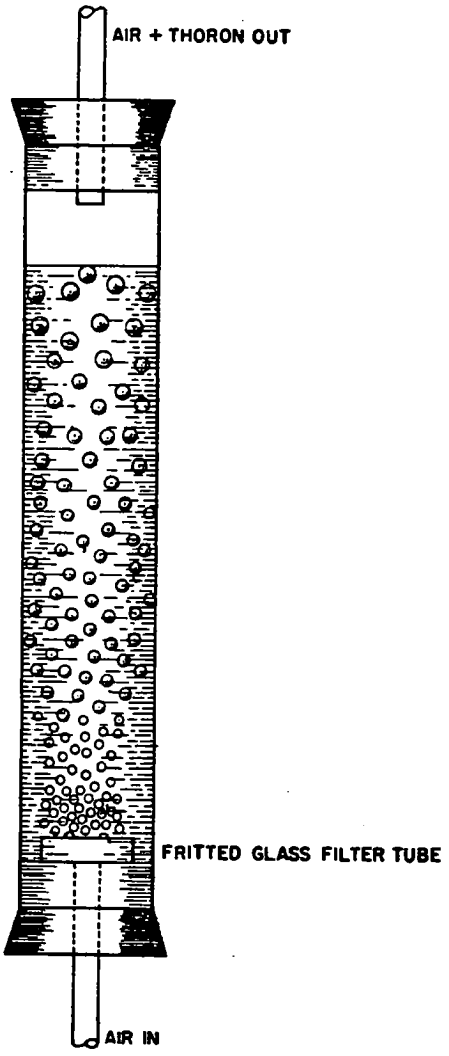


FIG. 2 — SAMPLE HOLDER

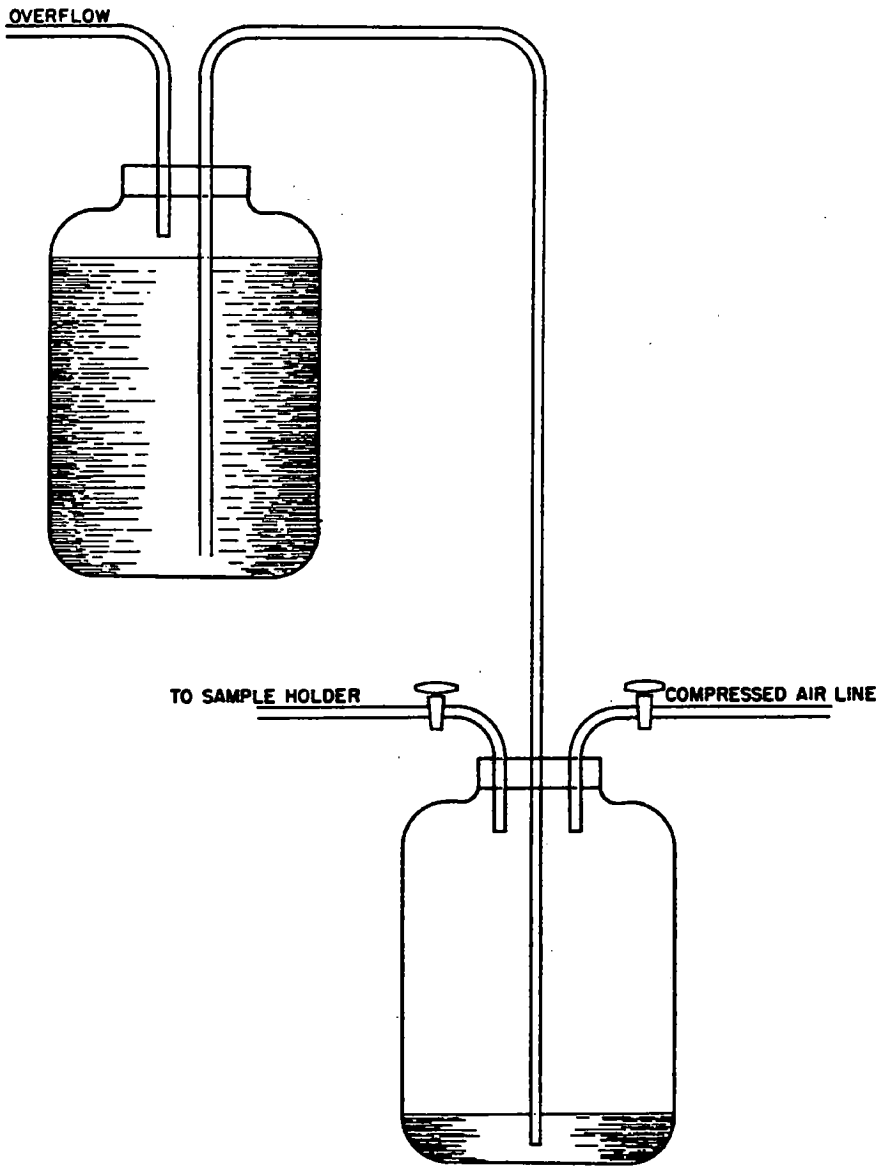


FIG. 3 — GAS PRESSURE SYSTEM

The scintillations from the phosphor are amplified by the photomultiplier tube and fed to a scaler, such as Nuclear Instrument Co. Model 182A.

After the apparatus has been set up (Figure 4), and a trial run made with a standard thorium solution, it is ready to be tested to determine the optimum working conditions.

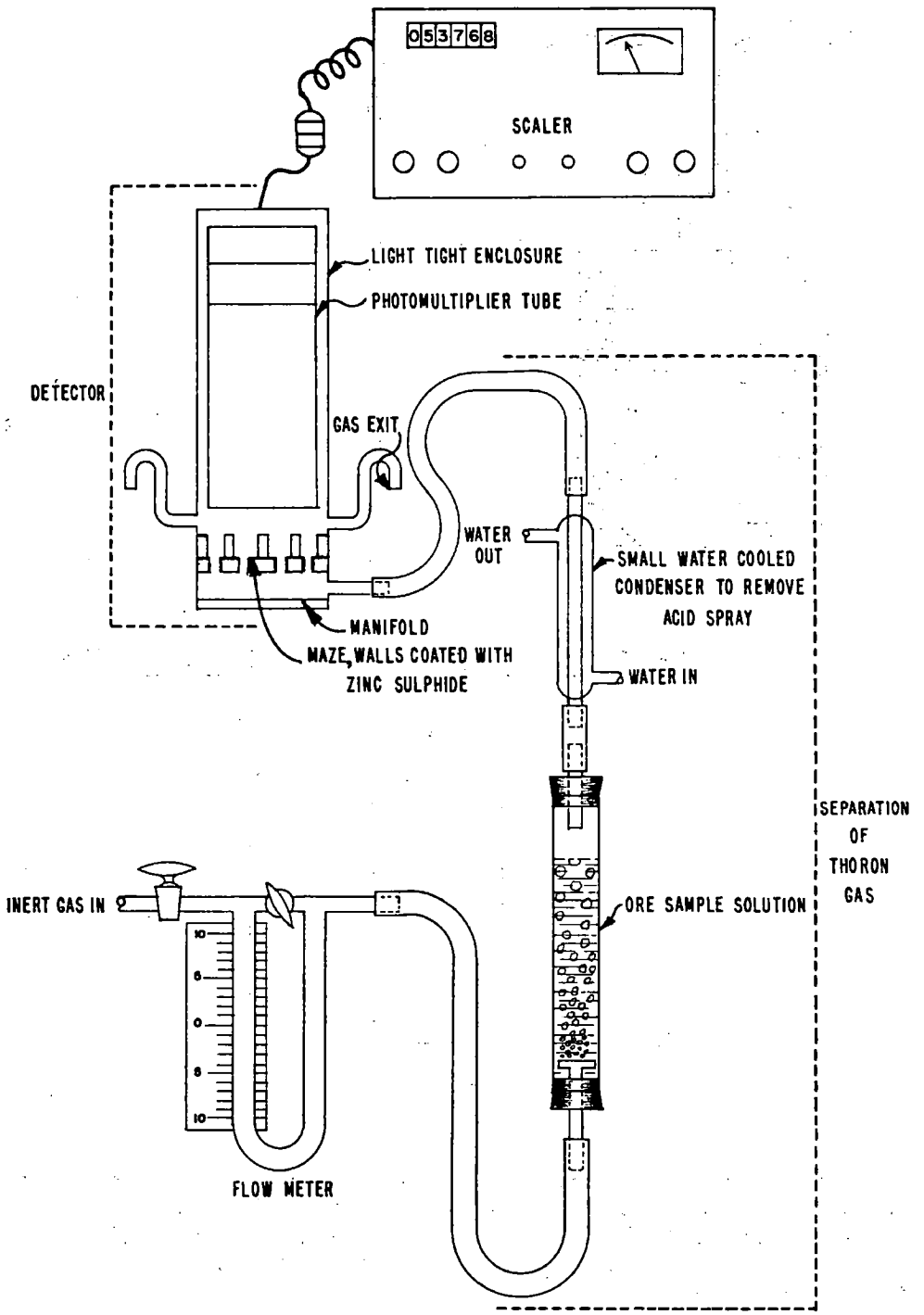


FIG. 4 – BLOCK DIAGRAM OF THORIUM EMANATION APPARATUS

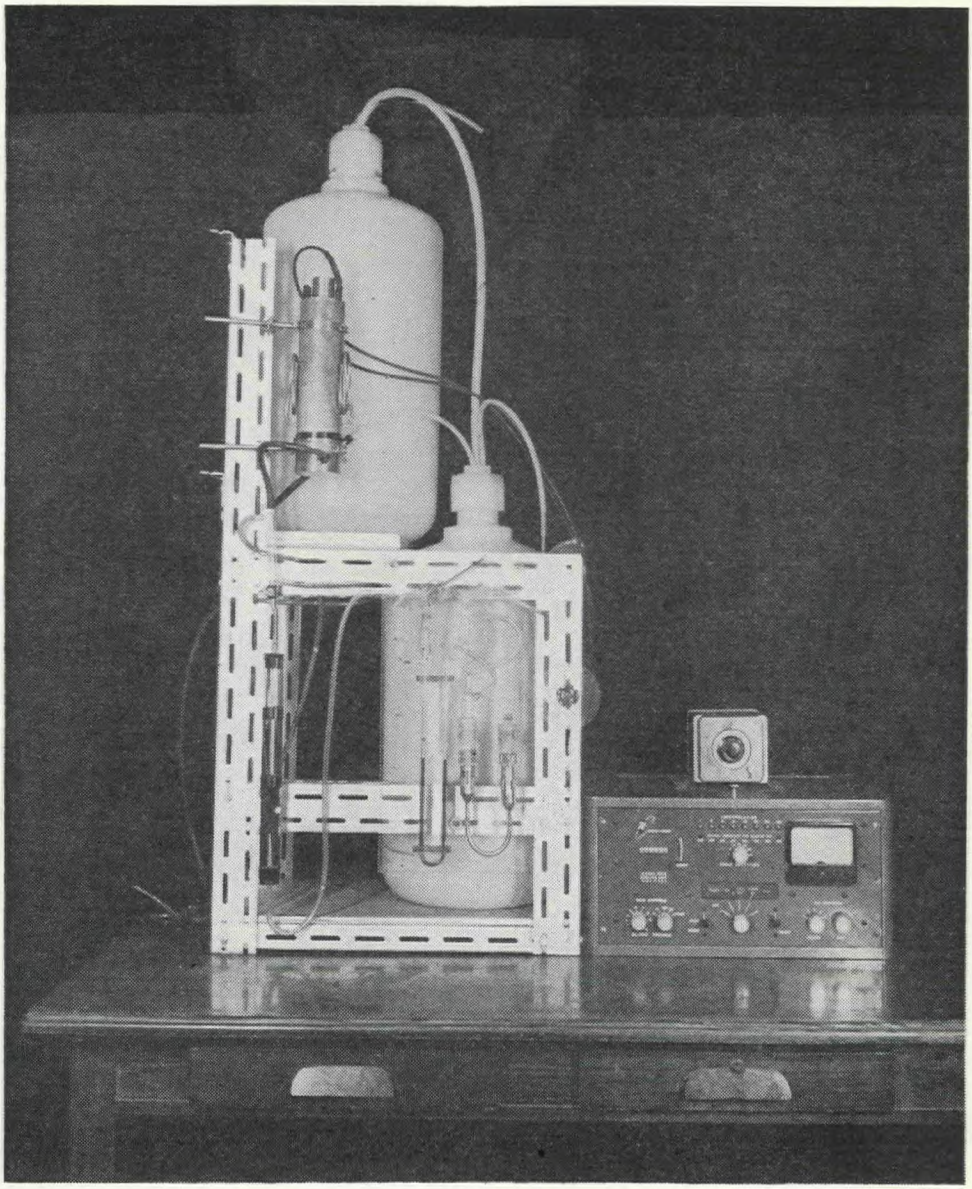


FIG. 5—THORIUM EMANATION APPARATUS

It is quite apparent that the short half-life of thoron (54.5 seconds) makes it impossible to take a lengthy observation on a stationary volume of gas. The gas sample must, therefore, be fed continuously in a steady stream to the scintillator from the sample, where it is being produced continuously by the disintegration of thorium X, a decay product of thorium. The rate at which

the steady stream of gas arrives at the scintillator is important. A rate which is too slow would allow most of the thoron atoms to decay before reaching the scintillator and too fast a rate would cause most of the thoron atoms to pass

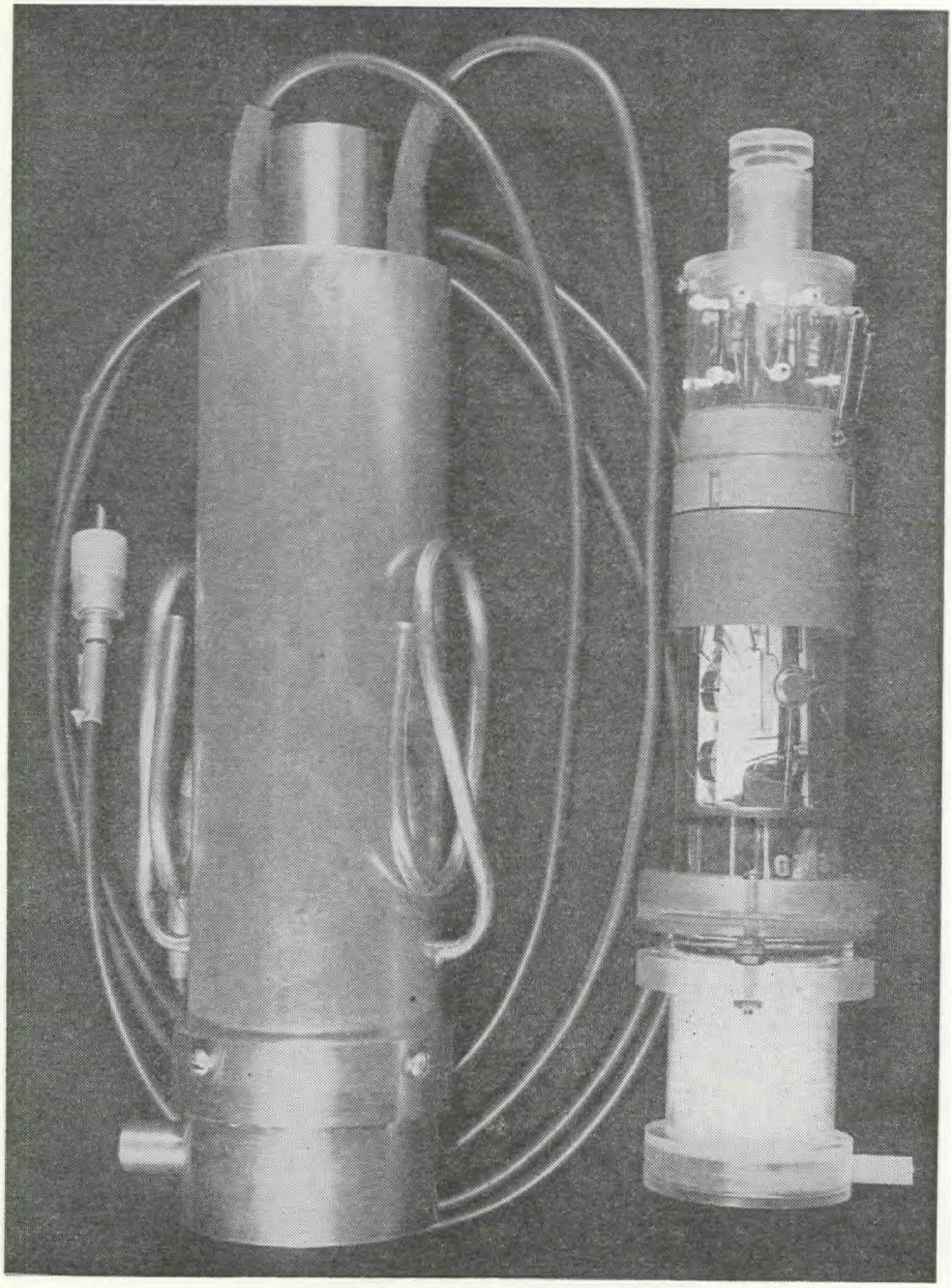


FIG. 6—PHOSPHOR-PHOTOMULTIPLIER COMBINATION

through the scintillator before disintegration. Optimum flow rate can be determined mathematically (4), from the parameters of the flow system, by using the formula:

$$F_{max} = \frac{\lambda V_1}{\log_e \left(1 + \frac{V_1}{V_2}\right)}$$

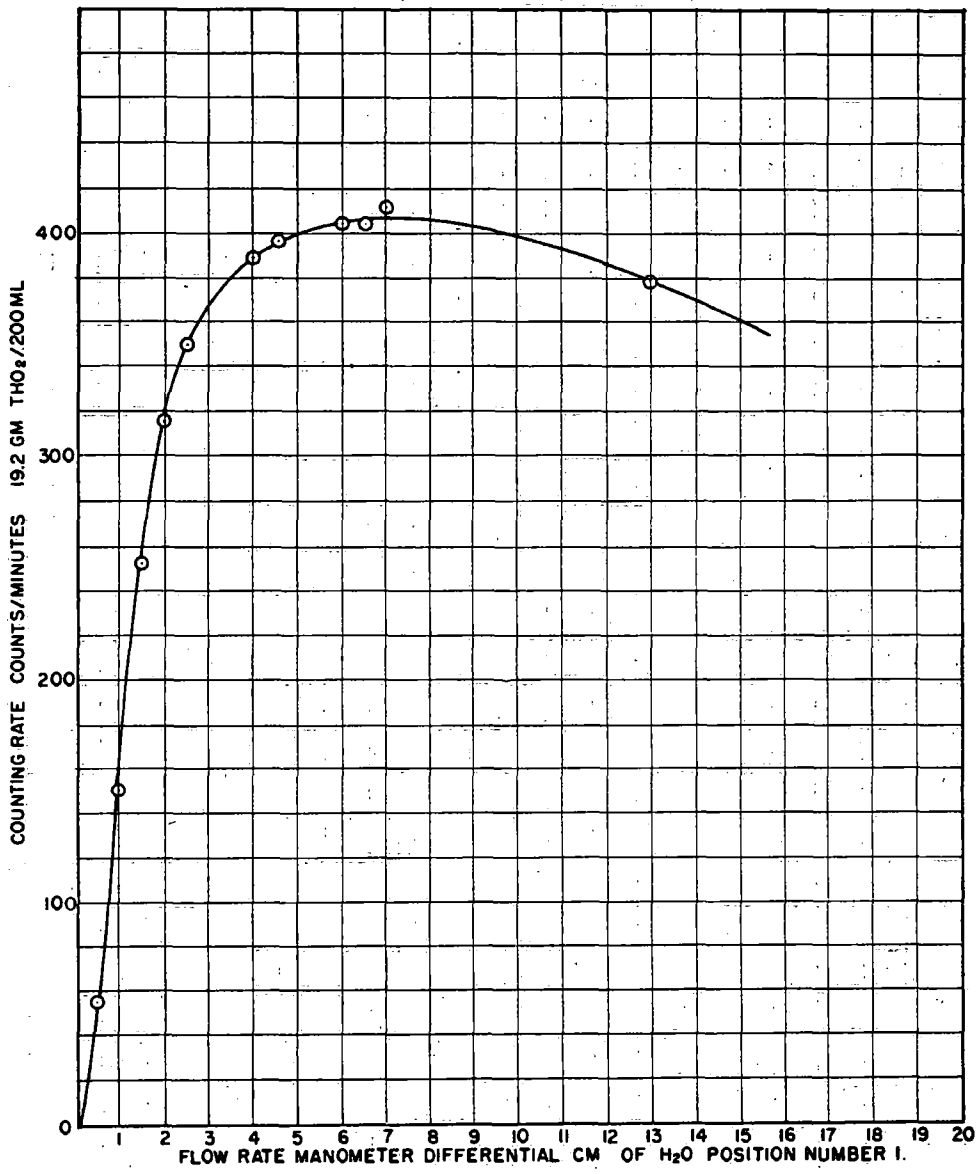


FIG. 7 — THORON FLOW CURVE

where λ is the decay constant for thoron, V_1 is the volume of the scintillator chamber, and V_2 the volume of the system from the surface of the solution in the sample holder to the scintillator.

A more practical way to determine the maximum flow is to draw a flow curve (Figure 7) by varying the rate of flow of air through the sample and plotting the count rate registered by the scaling unit vs. flow-meter reading. The flow curves have a characteristic broad top which allows considerable variation on each side of the optimum flow rate.

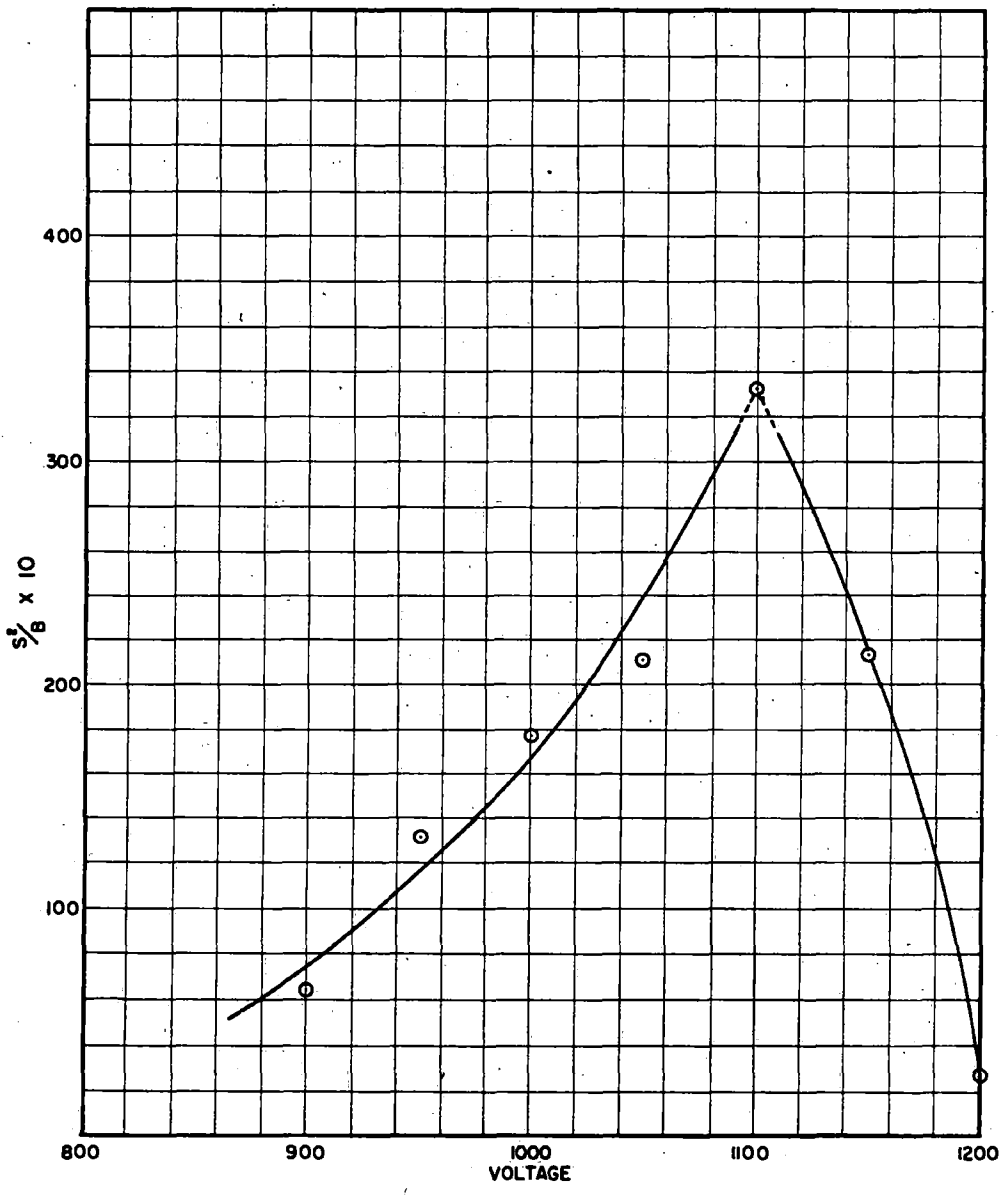


FIGURE 8 — OPTIMUM VOLTAGE SETTING

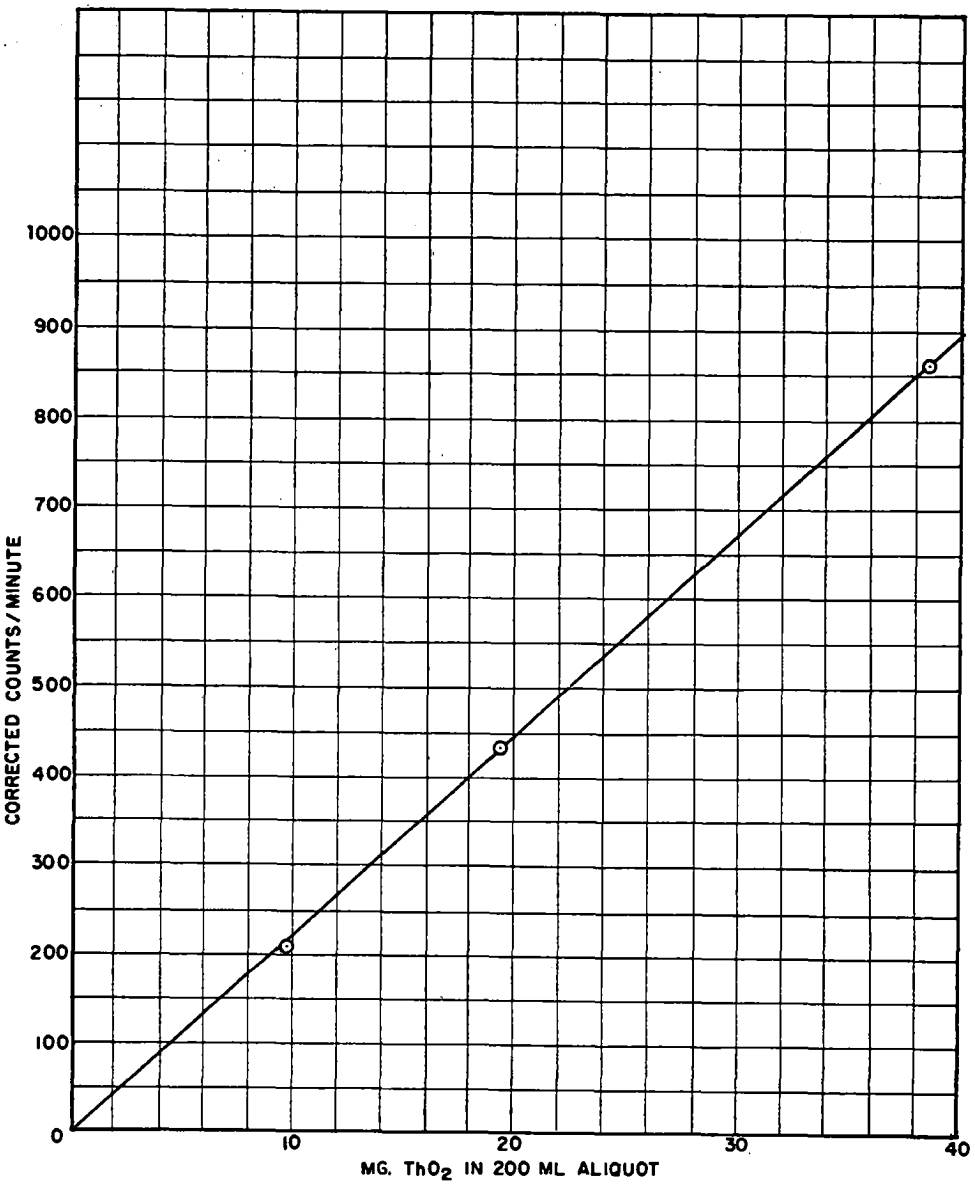


FIG. 9—CALIBRATION CURVE

The detecting system can be operated at its greatest sensitivity by increasing the voltage applied to the photomultiplier tube. However, there is a limit to which the voltage can be raised and still distinguish counts due to thoron, as the noise level of photomultiplier tubes increases with increased voltage, thus raising the background count.

If a plot of S^2/b vs. V is drawn (where "S" = corrected counts/minute due to the sample, "b" = counts/minute due to background, and "V" = voltage applied to the photomultiplier tube, there is a point where the ratio begins to decrease with increasing voltage (Figure 8). The voltage at this point produces optimum sensitivity for the particular photomultiplier tube used in the instrument when the scaling-unit controls are kept at a constant setting.

After optimum operating conditions have been established, calibration is carried out by running different amounts of a thorium standard and drawing a

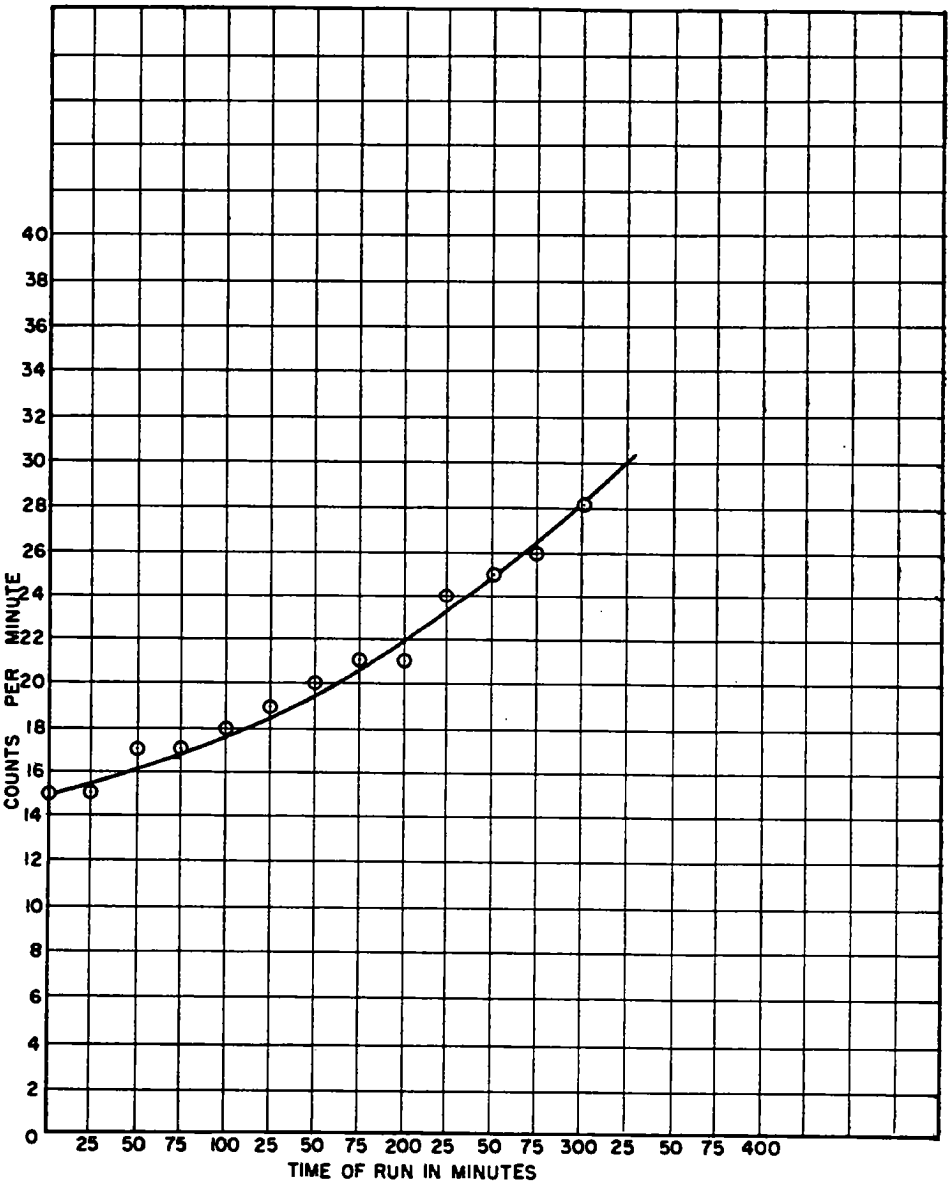


FIG. 10—INCREASE IN BACKGROUND COUNTING RATE

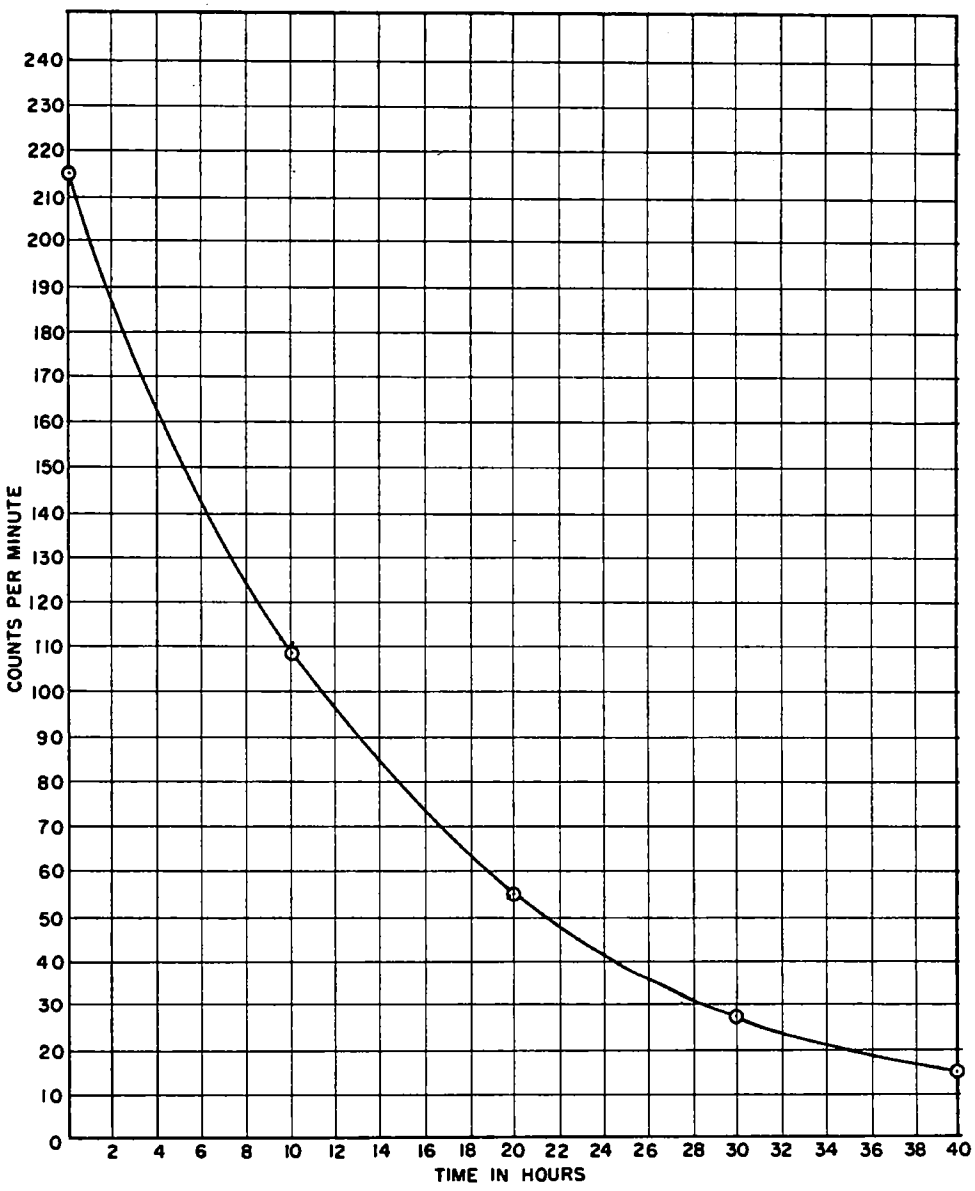


FIG. II — DECAY OF HIGH BACKGROUND WITH HALF LIFE OF ThB

graph of net counts/minute due to sample vs. thorium content in milligrams ThO_2. A typical curve is shown in Figure 9. In practice a standard sample is run each day to check the calibration. A continuous run of samples and standards will produce a gradual increase in the background counting rate. Figure 10

shows such an increase due to 19.2 mg ThO_2. The emanation from this amount contacted the phosphor for 105 minutes out of a total run time of 300 minutes.

The background count above that due to natural disintegrations within the phosphor is due to alpha rays produced in the disintegration of thorium C^I and C^{II}, daughter products of thoron which have very short half-lives of 0.3 micro-seconds and 3.1 minutes respectively. These two alpha-emitting elements quickly reach equilibrium with the longest-lived member left after the disintegration of thoron, and decay with the half-life of thorium B, i.e. approximately 10.6 hours. This is shown in Figure 11, which is a plot of the background decay from a highly contaminated phosphor.

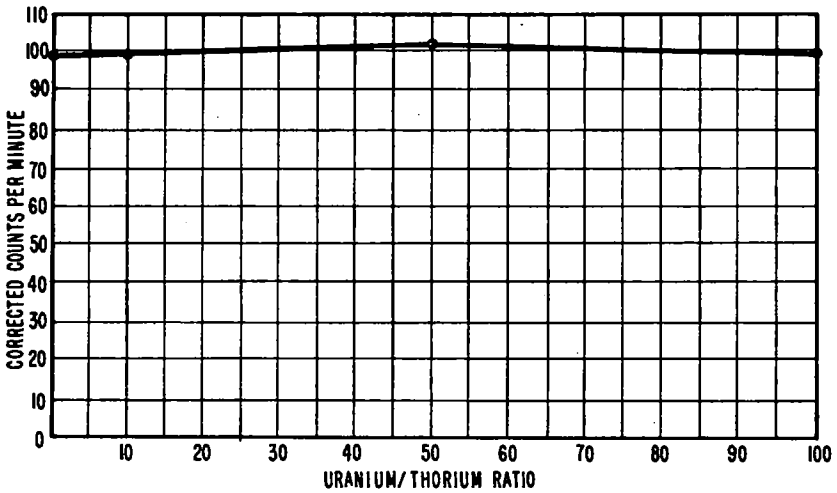


FIG. 12 - INDEPENDENCE OF THORIUM COUNTING RATE ON URANIUM CONTENT OF SAMPLE

5. REAGENTS

Hydrochloric acid, concentrated:	
Nitric acid, concentrated:	
Hydrofluoric acid, concentrated:	Reagent 48%.
Perchloric acid, concentrated:	
Hydrogen peroxide:	Reagent 30%.
Hydroxylamine hydrochloride:	
Potassium fluoride, anhydrous:	KF.
Sugar charcoal:	
Hydrofluoric acid wash solution, 16%:	1 part of concentrated (48%) acid to 2 parts of water.
Hydrofluoric acid wash solution, 2%:	1 part of concentrated (48%) acid to 23 parts of water.
Aluminum nitrate salting solution:	190 gm $Al_2(NO_3)_3 \cdot 9H_2O$, 85 ml water and 15 ml concentrated nitric acid. Warm to dissolve. Keep in a covered container in a warm place, but cool before using.

Mesityl oxide-hexane mixture:	950 ml mesityl oxide and 50 ml hexane.
Nitric acid 10%, v/v:	10 ml concentrated nitric acid to 100 ml with water.
Nitric acid 5%, v/v:	
Lanthanum nitrate solution:	20 gm $La(NO_3)_2.6H_2O$ in 1 litre of 5% nitric acid. 1 ml ≑ 10 mg La_2O_3.
Saturated borax solution:	for treating HF burns.
"Aged" thorium nitrate solution:	For Thorium Emanation method only. *Do not use as colorimetric standards.* Prepare a solution containing 20 mg ThO_2 as nitrate in 200 ml 1% nitric acid solution. Use a thorium nitrate or oxide that has been prepared more than 30 years ago. Standardize the solution gravimetrically by pipetting a suitable aliquot into a beaker and evaporating to low volume. Transfer to an ignited and tared crucible, evaporate to dryness, ignite at 1100° C to constant weight.
Sebacic acid-methanol solution:	50 gm sebacic acid in 1 litre of 99% methanol.
Methyl oxalate-methanol solution:	500 gm methyl oxalate in 1 litre of 99% methanol.
Thorin solution, 0.375% aqueous:	3.75 gm 2-(2 hydroxy-3, 6 disulpho-1 naphthyl azo)-benzene arsonic acid in 1 litre of water.
Hydroxylamine hydrochloride solution, 5%:	50 gm $NH_2OH.HCl$ per litre of water.
Thorium solution, colorimetric standard:	Dissolve 10.0 gm reagent thorium nitrate (*not* the aged material used for emanation standards) in 25 ml of 5% nitric acid and make to 1000 ml. Determine the ThO_2 content by pipetting an aliquot containing at least 50 mg ThO_2 into an ignited and tared platinum crucible, and weighing the residue left after drying and igniting to constant weight at 1100° C.

Preparation of Colorimetric Calibration Graph (for Section 6.d.1.)

Carry through a blank. Pipette aliquots of the thorium colorimetric standard solution containing from 100 to 3000 micrograms of ThO_2 into 250-ml beakers and dilute to 100 ml with water. Neutralize with ammonium hydroxide until the solution just becomes permanently turbid then add 5.0 ml concentrated hydrochloric acid. Transfer to a 250-ml volumetric flask, add 10 ml of 0.375% Thorin reagent solution and make to volume at room temperature. Read the optical density of the solutions at 545 mμ in 1-cm and 5-cm Corex cells on the Beckman Model B spectrophotometer against a blank carried through the above procedure. Plot a graph with optical density as abscissa and micrograms ThO_2 per 250 ml volume as ordinate, for both cell path-lengths.

Preparation of Colorimetric Calibration Graph (for Section 6.d.2.)

Carry through a blank. Take aliquots of the thorium colorimetric standard solution containing from 100 to 3000 micrograms of ThO_2. Add 5 ml of perchloric acid and fume to dryness. Redissolve in 5 ml of 5% concentrated hydrochloric and 25 ml of water. Add 10 ml of 5% hydroxylamine hydrochloride solution and boil 3 or 4 minutes. Cool to room temperature and transfer to 250-ml volumetric flasks. Add 10 ml of 0.375% Thorin solution and dilute to volume.

Read the optical density of the solutions at 545 mμ, in 1-cm and 5-cm Corex cells, on the Beckman Model B spectrophotometer, against a blank carried through the above procedure. Plot a graph with optical density as abscissa and micrograms ThO_2 per 250 ml volume as ordinate, for both cell path-lengths.

6. PROCEDURE—OUTLINES OF ANALYTICAL SCHEMES

To reduce the number of separate procedures required, this method covers a large number of dissimilar materials by using various combinations of a small number of steps. The following list summarizes the materials encountered and the steps used to treat them.

1. Ores, combined emanation and colorimetric procedure, Sections 6.a.1, 6.b, 6.c, 6.d.1.
2. Samples low in zirconium, titanium, niobium, and tantalum, containing less than 0.1% ThO_2, Sections 6.a.2, 6.b, 6.d.2.
3. Samples high in zirconium, titanium, niobium, and tantalum, containing more than 0.05% ThO_2, Sections 6.a.3, 6.c, 6.d.1.
4. Samples containing more than 0.1% ThO_2, Sections 6.a.4, 6.c, 6.d.1 or 6.e.
5. Samples containing large amounts of calcium sulphate (gypsum cake) and/or rare earths, Sections 6.a.5, 6.b, 6.d.2.
6. Thorium oxalate and hydroxide precipitates containing 25% ThO_2 or more, Sections 6.a.6, 6.b, 6.e.
7. Kerosene-amine solutions, Section 6.a.7, 6.b, 6.d.2.
8. Organic extractants, general procedure, Sections 6.a.8, 6.b, 6.d.2.
9. Aqueous leach liquor and strip solutions, Sections 6.a.9, 6.b, 6.d.2.

6.a. Preliminary Preparation

6.a.1. *Decomposition and Thorium Emanation Determination, for ores only.*

Weigh a suitable sample of the ore (up to 5 gm) into a 150-ml platinum dish, moisten with about 3 ml of water, and transfer to a fume hood. Wearing safety glasses and rubber gloves, cautiously add 25 ml of concentrated hydrofluoric acid. Evaporate to near dryness at low heat. Twice more, add 25-ml portions of hydrofluoric acid, stir well with a nickel stirring rod and take almost to dryness, using a higher temperature (since spattering is less likely). Using a minimum of water, transfer the contents of the platinum dish quantitatively to a 250-ml beaker. Cautiously add 20 ml concentrated nitric acid and 20 ml concentrated perchloric acid. Evaporate just to fumes, then cover with a watch glass and reflux in the perchloric acid for 5 minutes. Remove the watch glass and evaporate nearly to dryness. Cool, add 75 ml of 10% nitric acid and boil to dissolve. If a reddish brown residue (iron) remains, add 1 gm of hydroxylamine hydrochloride and continue boiling. A grey-white residue may be a titanium compound. In this case add 5 ml hydrogen peroxide and boil gently.

Filter off any residue remaining on a small Whatman No. 42 paper and reserve the filtrate. Dry and ignite the paper in a 30-ml platinum crucible, and fuse with 5 gm sodium carbonate. Cool the crucible, transfer to a 250-ml beaker and cautiously dissolve the melt in 25% nitric acid. Combine this solution with the reserved filtrate. Adjust the sample volume to 200 ml.

Boil the solution to "de-emanate" (i.e. drive off accumulated radon from the uranium series). While this is being done, determine the initial background reading, carry out a standard determination using the standard aged thorium nitrate solution, then rinse the sample holder well and make a second background

determination. Finally, adjust the flow of air to provide enough pressure to prevent diffusion of the sample through the glass frit and transfer the sample quantitatively to the sample holder. Insert the upper stopper in the sample holder and adjust the flow of air through the solution to the same value used in calibration and standardization. Let air bubble through the solution for 5 minutes without counting, then record the number of counts over a period of time that will provide a sufficient number to give the statistical level of significance required (17) and calculate the number of counts per minute. Transfer the solution quantitatively to a 600-ml beaker. Rinse the sample holder thoroughly and again take a background determination. Correcting both standard and sample for background counts, calculate the thorium content of the sample from their ratio.

Proceed with the sebacic acid (6.b) and mesityl oxide (6.c) separations on the solution used for this determination and complete colorimetrically as described in Section 6.d.1.

6.a.2. *Decomposition and Preliminary Treatment (if Emanation Determination Not Required), Samples Low in Zirconium, Titanium, Niobium and Tantalum, Containing Less than 0.1% ThO_2.*

Weigh a suitable portion of the sample containing 1 to 50 mg ThO_2 (up to 5 gm) into a 150-ml platinum dish, moisten with about 3 ml of water, and transfer to a fume hood. Wearing safety glasses and rubber gloves, cautiously add 25 ml of concentrated hydrofluoric acid. Evaporate to near dryness at low heat. Twice more, add 25-ml portions of hydrofluoric acid, stir well with a nickel stirring rod and take almost to dryness, using a higher temperature (since spattering is less likely). Finally add a 10-ml portion of hydrofluoric acid, followed by 30 ml of water, and heat on a steam bath for 10-15 minutes.

Cool the solutions, add 1 ml lanthanum nitrate solution and stir well with a nickel rod. Transfer completely to modified 8-oz. polyethylene centrifuge bottles, let stand at least 1 hour, and centrifuge for 15 minutes at 2000 r.p.m. Decant and discard the supernatant liquid. Add 50 ml 2% hydrofluoric acid wash solution to the polyethylene bottles, stir well, centrifuge and again discard the supernatant solution.

Transfer the insoluble fluorides to a 250-ml glass beaker and add 10 ml concentrated nitric acid and 15 ml concentrated perchloric acid. Evaporate to near dryness and redissolve by boiling with 75 ml of 5% nitric acid. If a residue remains, filter it off into a 600-ml beaker, using a small Whatman No. 42 paper, and reserve the filtrate. Dry the paper and residue, and ignite in a 30-ml platinum crucible. Fuse with 5 gm sodium carbonate, transfer the crucible to a 250-ml beaker and cautiously dissolve the melt in a minimum of 25% nitric acid. Combine the filtrates in the 600-ml beaker and adjust the volume to about 200 ml.

Then treat the solution by the sebacic acid method, Section 6.b, and complete the determination colorimetrically using the method given in Section 6.d.2.

6.a.3. *Decomposition and Preliminary Treatment, Samples High in Zirconium, Titanium, Niobium and Tantalum, Containing More than 0.05% ThO_2.*

Weigh a suitable portion of the sample (up to 2 gm) into a 150-ml platinum dish, and moisten with 3 ml of water. Transfer to a fume hood, and wearing

safety glasses and rubber gloves, cautiously add 25 ml of hydrofluoric acid. Evaporate at low heat on a heavily padded hot plate until not quite dry. Add a second 25-ml portion of hydrofluoric acid, stir well with a nickel stirring rod, and again take almost to dryness (heating more strongly than before). Add 10 ml of concentrated hydrofluoric acid followed by 30 ml of water and heat on a steam bath for 15 minutes to dissolve the soluble fluorides.

Cool to room temperature and transfer to 8-oz polyethylene bottles. Stirring the solution vigorously, add 1 ml of lanthanum nitrate solution. Let stand at least 1 hour, then centrifuge the samples for 15 minutes. Discard the supernatant solution. Transfer the insoluble fluorides to the original platinum dish, evaporate to near dryness and add 60 gm of anhydrous potassium fluoride. Cover with a thin layer of sugar charcoal and fuse over a Fisher blast burner using propane gas for 2 minutes or until the melt becomes clear. (Do not fuse for an excessively long time to avoid the formation of thorium oxyfluoride which is difficult to redissolve.) Cool, add 80 ml of hydrofluoric acid and digest under infra-red lamps in a well-ventilated hood for at least 30 minutes or until the melt has completely redissolved, except for the insoluble thorium, rare earth and calcium fluorides.

Transfer the hot fluoride mixture to 8-oz. polyethylene bottles and centrifuge for 3 minutes. Discard the supernatant liquid and add 100 ml of hot 16% hydrofluoric acid solution. Stir, centrifuge for 3 minutes and discard the supernatant liquid. Add 20 ml of aluminum nitrate salting solution and heat on the steam bath to dissolve the fluorides. Stir occasionally, cool to room temperature and continue with the mesityl oxide separation (6.b) omitting the sebacic acid precipitation step. Complete according to Section 6.d.1.

6.a.4. *Decomposition Method for Ores, Concentrates and Residues Containing more than 0.1% ThO_2.*

Weigh out a suitable portion of the sample, containing 1 to 50 mg ThO_2 (0.1 to 1 gm), and all ground to −200 mesh, into a 150-ml platinum dish. Moisten with water and add lanthanum nitrate solution equivalent to 4.0 mg La_2O_3. Transfer to a fume hood, and wearing safety glasses and rubber gloves, slowly and cautiously add 20 ml of concentrated hydrofluoric acid. Place on a heavily padded portion of the hot plate and carefully evaporate almost to dryness taking care to avoid spattering. Repeat the hydrofluoric acid treatment, evaporating at a higher temperature, until not less than 2 ml of hydrofluoric acid remains. Now add 60 gm anhydrous potassium fluoride, cover with a thin layer of sugar charcoal, and fuse over a Fisher blast burner burning propane gas for 2 minutes, or until the melt becomes clear. (Do not fuse for an excessively long period of time, since thorium oxyfluoride, which is difficult to redissolve, may be formed.) Cool, add 80 ml of hydrofluoric acid, and digest under infra-red lamps in a well-ventilated hood for at least 30 minutes or until the melt has completely dissolved, leaving only the insoluble fluorides of thorium, rare earths and calcium. Break up the melt during digestion.

Transfer the hot fluoride mixture to 8-oz. polyethylene bottles and centrifuge for 3 minutes. Decant and discard the supernatant liquid. Stir the precipitate with 100 ml of hot 16% hydrofluoric acid solution, centrifuge, and again discard the supernatant liquid.

Proceed to Section 6.c "Mesityl oxide separation", omitting Section 6.b "Sebacic acid separation", and complete according to Section 6.d.1.

6.a.5. *Decomposition and Preliminary Treatment of Samples containing Large Amounts of Calcium Sulphate (Gypsum Cake) and/or Rare Earths*

Weigh a portion of the sample containing not less than 0.5 mg of ThO_2 into a 250-ml beaker. Add 5 ml of nitric acid, 10 ml of perchloric acid and 10 ml of lanthanum carrier. Transfer to a hot plate and evaporate nearly to dryness. Add 5 ml of concentrated nitric acid, followed by 25 ml of water, and boil to redissolve. Dilute to 100 ml, add 0.5 gm hydroxylamine hydrochloride and cool to room temperature. Adjust to pH 10 using concentrated ammonium hydroxide followed by a 5-ml excess. Add a small amount of paper pulp and let stand 1 hour. Filter on a Whatman No. 41H filter paper and discard the filtrate.

Transfer the paper and precipitate to the original beaker. Evaporate several times with nitric acid to destroy the bulk of the organic matter. Finally add 10 ml nitric acid and 10 ml of perchloric acid and evaporate almost to dryness.

Add 5 ml concentrated nitric acid, stir to dissolve, and take up in 25 ml water. Transfer to a 600-ml beaker, adjust the volume to 200 ml and proceed with Sections 6.b. and 6.d.2. (Omit the mesityl oxide separation, Section 6.c.)

6.a.6. *Decomposition of Thorium Oxalate and Hydroxide Precipitates Containing 25% ThO_2 or More.*

Weigh out portions (e.g. 5 gm) sufficient to be representative of the whole sample, into tared, 12-ml glass-stoppered weighing bottles which have been allowed to come to equilibrium in the balance case. Do not take the time to weigh out a stated amount, but measure out the required amount approximately, as rapidly as possible, using a suitable measuring spoon. If the result is to be reported on the dry basis, weigh out a sample for moisture determination at the same time (METHOD M-1). Immediately stopper both the sample bottle and weighing bottles, and weigh the weighing bottles exactly, determining the sample weight taken by difference. Transfer to a 400-ml beaker, rinsing the bottle with water, then dilute nitric acid (1:1 v/v) and finally scrubbing with a rubber policeman.

Add 50 to 75 ml of concentrated nitric acid. Cover with a watch glass and digest for 1 hour under infra-red lamps, stirring occasionally. If the sample does not dissolve completely, transfer to a hot plate, remove the watch glass and boil until complete solution is obtained.

If a residue of silica remains, filter it off and reserve the filtrate. Dry the paper and ignite it in a 60-ml platinum dish. Add 10 ml hydrofluoric acid and take to dryness. Repeat this treatment, then slurry the residue in 20 ml of nitric acid and transfer to a 250-ml beaker. Add 20 ml perchloric acid and take to fumes. Cover and let reflux for 15 minutes. Cool, dilute with 50 ml water and combine with the original filtrate. Transfer the solution to a 500-ml volumetric flask and dilute to volume at room temperature.

Pipette a suitable aliquot containing 50-100 mg ThO_2 into a 600-ml beaker and dilute to 200 ml. Carry out a sebacic acid separation (Section 6.b) and complete gravimetrically (Section 6.e).

6.a.7. *Stripping and Preliminary Treatment of Kerosene-Amine Solutions*

Pipette a suitable aliquot (10-50 ml) of the organic solution into a 125-ml separatory funnel. Add 2 ml of 10% sodium carbonate for every 10 ml of

organic solution taken. Shake the funnel for 1 minute, then allow the phases to separate. Run the aqueous phase into a 250-ml beaker. Add a further 2 ml of sodium carbonate to the separatory funnel.

Do not shake the funnel, but simply drain this solution out to rinse the stem of the funnel. Finally wash the stem with water. Repeat the entire stripping procedure three times.

Cautiously neutralize the solution in the beaker with concentrated nitric acid. Add about 5 ml of nitric acid in excess and transfer the solution to a 100-ml volumetric flask. Pipette a suitable aliquot (containing at least 500γ) into a 600-ml beaker, add 10 ml of concentrated nitric acid and evaporate to dryness under the infra-red lamps. Add 10 ml of concentrated nitric acid, followed by 10 to 20 ml of concentrated perchloric acid, and fume almost to dryness. Add 5 ml of nitric acid, followed by 25 ml of water and warm to dissolve. Adjust the volume to 200 ml and proceed with Section 6.b followed by Section 6.d.2.

6.a.8. *Preliminary Treatment of Organic Extractants—General Method (Other Suitable Procedures will be Found in Method U-1 and Method U-4)*

Pipette a suitable aliquot into a Coors No. 1A porcelain crucible. Insert a 1″ long piece of twisted filter paper (½″ wide) to serve as a wick. Place in a fume hood and ignite. Let burn until the organic matter is completely consumed and only carbon remains. (Replace the wick if necessary.) Finally burn off the carbon by putting the crucible in a hot muffle (400-600° C) for 2 or 3 minutes. Remove, and let cool. Add 10 ml nitric acid and a drop of 1:40 (v/v) hydrofluoric acid, and warm to dissolve. Transfer to a 600-ml beaker. Repeat this nitric acid-hydrofluoric acid treatment twice more. Evaporate the solution in the beaker almost to dryness, then take up in 5 ml nitric acid and 25 ml water. Dilute to 200 ml, and proceed with Section 6.b followed by Section 6.d.2.

6.a.9. *Preliminary Treatment of Aqueous Leach Liquor and Strip Solutions*

Pipette a suitable aliquot of the solution (containing not less than 0.5 mg ThO_2) into a 250-ml beaker. Add 5 ml nitric acid, 10 ml perchloric acid, and 10 ml lanthanum carrier solution, and fume the sample nearly to dryness. Add 5 ml of concentrated nitric acid and 25 ml water, and boil to redissolve. Dilute to 100 ml, add 0.5 gm hydroxylamine hydrochloride and cool to room temperature. Adjust to pH 10 with ammonium hydroxide, then add 5 ml excess. Add a small amount of paper pulp and digest for 1 hour. Filter through a Whatman No. 41 H filter paper. Discard the filtrate.

Transfer the paper and precipitate to the original beaker. Fume nearly to dryness with 10 ml nitric acid and 10 ml perchloric acid. Take the perchlorates up with 5 ml of concentrated nitric acid and 25 ml water. Transfer to a 600-ml beaker, dilute to 200 ml, and proceed with Sections 6.b. and 6.d.2.

6. b. Sebacic Acid Separation

To the solution from Sections 6.a.1, 6.a.2, 6.a.6, 6.a.7, 6.a.8 and 6.a.9, in a 600-ml beaker, volume about 200 ml, add 1 gm of hydroxylamine hydrochloride. Heat on a steam bath for 15 minutes. Add ammonium hydroxide until a permanent precipitate just begins to form. Cool the solution to room temperature and adjust the pH to 2.6 by means of a pH meter, using ammonium hydroxide or nitric acid. Add 20 ml of sebacic acid solution and boil for 3 minutes. Transfer the samples to the steam bath, add 5 ml of methyl oxalate solution and digest the solution for 15 minutes. Add paper pulp and filter hot through a Whatman No. 50 filter paper using the Fisher filtrator. Wash the precipitate five times using boiling water and adjust to pH 2.6 with dilute nitric acid.

For high-grade samples (Section 6.a.6), see Section 6.e (gravimetric finish).

For other samples, return the precipitate and filter paper to the original beaker. Evaporate to dryness several times with nitric acid to destroy the bulk of the organic matter. Finally fume to dryness with 10 ml of concentrated nitric acid and 10 ml of concentrated perchloric acid.

If proceeding directly to the colorimetric finish, (Section 6.d.2., for gypsum cake and rare earth concentrates), add 50 ml water and warm to dissolve. Cool, transfer to a 100-ml volumetric flask and make to volume at room temperature. If the whole sample is being used for colour development, transfer to a 250-ml beaker.

6. c. Mesityl Oxide Separation

Carry suitable standards through the subsequent procedure to verify recovery.

To the residue in the polyethylene bottle or glass beaker (Section 6.a.3 or 6.a.4) add 20 ml of aluminum nitrate salting solution. Place the container on the steam bath, cover with a watch glass, and warm to dissolve. When the residue is completely dissolved, cool to room temperature. Transfer the solution (take only one at a time) to a 125-ml separatory funnel. (The extractions must be carried out rapidly to avoid charring of the mesityl oxide). Add 20 ml of the mesityl oxide-hexane mixture to the original bottle, swirl and transfer to the separatory funnel. Stopper with a No. 1 polyethylene stopper and shake vigorously for about 20 seconds (but no longer). Let the phases separate and quickly transfer the aqueous phase to a 60-ml separatory funnel. Again add 20 ml of the mesityl oxide-hexane mixture and shake for 20 seconds. Let the layers separate and discard the aqueous layer. Run the organic layer from the 60-ml separatory funnel into the 125-ml funnel and scrub the combined organic layers with 20 ml of aluminum nitrate scrub solution i.e. stopper and shake the funnel for 20 seconds, let the layers separate and discard the aqueous layer. Repeat this scrubbing three times. Finally let the funnel stand for 15 minutes, and draw off and discard any aqueous solution that settles out.

Strip the thorium from the mesityl oxide with four successive 20-ml portions of water. Transfer the water to a 100-ml volumetric flask and make up to volume immediately. If the complete sample is to be used, collect the stripping, containing 1500 micrograms of thorium if possible, in a 250-ml beaker and dilute to 100 ml.

6. d. Colorimetric Finish

6.d.1. *Colorimetric Finish (if mesityl oxide separation was carried out)*

NOTE: Carry through a reagent blank.

If only traces of thorium are being determined, or if only a small amount of sample was available, evaporate the entire sample solution to small volume and finish in 25-ml volumetric flasks, adjusting the volumes of reagents taken accordingly. Complete by reading in 5-cm cells.

For routine samples, take a suitable aliquot, neutralize with ammonium hydroxide until the solution just becomes permanently turbid, then add 5.0 ml concentrated hydrochloric acid. Transfer to a 250-ml flask, add 10 ml of 0.375% Thorin reagent solution and make to volume at room temperature.

Mix thoroughly and measure the optical density of the solutions, using the Beckman Model B spectrophotometer and 1-cm cells (or 5-cm cells if less than 100γ of ThO_2 was present in the aliquot taken for colour development) at a wave length of 545 millimicrons. Determine the micrograms of ThO_2 per 250 ml volume by means of a previously prepared calibration graph.

6.d.2. *Colorimetric Finish (if mesityl oxide separation was omitted).*

NOTE: Carry through a reagent blank.

If traces only are being determined, evaporate the entire sample solution to small volume and finish in 25-ml volumetric flasks. Adjust reagent volumes accordingly and read the solution in 5-cm cells.

For routine samples, pipette a suitable aliquot of sample solution containing 1000-1500γ ThO_2 into a 250-ml beaker. Evaporate just to dryness at low heat or on the steam bath. Take up in 5 ml concentrated hydrochloric acid and 25 ml water. Add 10 ml of 5% hydroxylamine hydrochloride and boil. Cool to room temperature and transfer to a 250-ml volumetric flask. Add 10 ml of 0.375% Thorin solution and make to volume.

Measure the optical density of the solution at 545 mμ on the Beckman Model B spectrophotometer against a blank carried through the complete procedure. Determine the micrograms of ThO_2 per 250 ml volume by means of a previously prepared calibration graph.

As an added precaution, carry three standards covering the 100 to 3000 microgram range through the complete procedure along with the samples. This is used to correct for slight manipulation losses.

6. e. Gravimetric Finish

Transfer the paper containing the precipitate from the sample (treated according to Section 6.a.6 and Section 6.b) to a tared 30-ml platinum crucible. Dry carefully on a hot plate, ignite over a low gas flame and finally ignite in a muffle furnace at 950° to 1000° C for 30 minutes. Transfer the ignited crucible to a desiccator containing an efficient desiccant, let cool for 30 minutes, record the weight of ThO_2 obtained and calculate % ThO_2.

7. CALCULATIONS

a) Colorimetric finish

$$\%\ ThO_2 = \frac{ThO_2,\ \gamma \text{ per } 250 \text{ ml}}{1{,}000{,}000} \times \frac{\text{final sol. vol.}}{\text{aliq. taken}} \times \frac{100}{\text{sample wt. gm}}$$

$$\text{gm/l } ThO_2 = \frac{ThO_2,\ \gamma \text{ per } 250 \text{ ml}}{1{,}000{,}000} \times \frac{\text{final sol. vol.}}{\text{aliq. taken}} \times \frac{1000}{\text{sample vol. ml}}$$

If the sample gives approximately the same reading as the blank, the amount of thorium should be reported as less than the minimum amount detectable (an actual figure based on the sample weight and volumes used). The minimum amount detectable may be considered as 750 micrograms ThO_2 per 250 ml volume (1-cm cell) or 150 micrograms ThO_2 per 250 ml volume using 5-cm cells, and the figure to report may be calculated on this basis, i.e.

$$\%\ ThO_2 = \text{less than } \frac{150\gamma}{1{,}000{,}000} \times \frac{\text{final solution volume}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

If a 25-ml dilution and 5-cm cells were used, the lower limit is reduced to 15γ ThO_2.

b) Gravimetric finish

$$\% \, ThO_2 = \frac{\text{wt. } ThO_2, \text{ gm}}{\text{sample wt.}} \times \frac{\text{final sol. vol.}}{\text{aliq. taken}} \times 100$$

$$\text{gm/l } ThO_2 = \frac{\text{wt. } ThO_2 \text{ gm}}{\text{sample vol. ml}} \times \frac{\text{final sol. vol.}}{\text{aliq. taken}} \times 1000$$

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17. METHOD Ra-1.

The Colorimetric Determination of Thorium Using Oxalate Precipitation with Lanthanum Carrier

METHOD Th-2

SCOPE

This method is intended to be used for the rapid determination of thorium in solutions or precipitates which do not contain large amounts of rare earths (1). Its principal use is for thorium in uranium concentrates for specification purposes. It is not intended for the general analysis of ores and other materials of unknown composition. For these materials, the sebacate or mesityl oxide methods are used.

RANGE

The range of the method is 0.01 to 15% ThO_2, in solid samples, and 0.005 gram per litre to 15 grams per litre ThO_2 in solutions.

OUTLINE

Thorium is precipitated from an acid solution (approx. 0.25 N in HCl) with oxalic acid using lanthanum as a carrier and NH_4OH for seeding to start the precipitation (2) (3). The quantitative insolubility of thorium oxalate has been the subject of a paper by Kall and Gordon (6), who found that in the presence of a rare earth carrier, losses were considerably reduced. Using 20 mg lanthanum oxide, and a procedure similar to that described here, 68 mg of ThO_2 was recovered with a loss of only 0.56 mg. Guest (2) was able to obtain quantitative recovery of as little as 22γ ThO_2, using 1 to 2 mg La_2O_3 as carrier.

The oxalate precipitate and filter paper are returned to the original beaker and fumed to near dryness with nitric and perchloric acids. The perchlorates are dissolved in dilute HCl, hydroxylamine hydrochloride is added to convert iron, cerium and uranium to non-interfering forms, and the thorium content is determined colorimetrically with Thorin reagent (4) (5). A discussion of the properties of this reagent will be found in METHOD Th-1.

APPARATUS

Pipettes, volumetric:	
Flasks, volumetric:	
Beakers, Griffin low form:	
Funnels, filtering, Bunsen long stem:	
Spectrophotometer:	Beckman Model B
Spectrophotometer cells:	Corex, 1-cm and 5-cm path-lengths

62314-0—14½

REAGENTS

Nitric acid, concentrated:	
Perchloric acid, concentrated:	
Hydrochloric acid, concentrated:	
Ammonium hydroxide, concentrated:	
Hydrochloric acid solution, 5%:	v/v.
Hydroxylamine hydrochloride solution, 5%:	5 gm $NH_2OH.HCl$ in 100 ml water.
Lanthanum solution, 1 ml = 10 mg. La_2O_3:	Dissolve 11.4 gm lanthanum chloride ($LaCl_3.7\ H_2O$) in water slightly acidified with hydrochloric acid. Make the solution up to 500 ml in a volumetric flask.
Oxalic acid:	Reagent grade $(COOH)_2.2H_2O$.
Wash solution, 2% oxalic acid:	
Thorin reagent:	0.375% Thorin in water. The B.D.H. reagent is preferable.
Standard thorium solution:	Dissolve 10.5 gm thorium nitrate ($Th(NO_3)_4 + H_2O$) in water slightly acidified with nitric acid. Make the solution up to 500 ml in a volumetric flask. Check the thorium content by an oxalate precipitation.

Preparation of Calibration Graph

Take aliquots of the thorium solution containing from 400 to 3000 micrograms of ThO_2. Add 1 ml of the lanthanum carrier solution and 1 ml of perchloric acid. Take to dryness. Redissolve in 5 ml of concentrated hydrochloric acid and make up to about 100 ml in a 250-ml volumetric flask. Add 10 ml of 0.375% Thorin reagent, and make up to volume. Read the optical density of the solution at 545 millimicrons on the Beckman Model B spectrophotometer against a blank solution prepared in exactly the same way except that no thorium is added. Plot a graph with optical density as abscissa and micrograms ThO_2 per 250 ml volume as ordinate, using 1-cm Corex cells. A similar curve should also be prepared using 5-cm cells, for use when increased accuracy is desired in the lower range.

PROCEDURE

Weigh a sample of precipitate, or take an aliquot of solution estimated to contain not less than 0.5 mg of ThO_2. Add 10 ml nitric acid and 10 ml perchloric acid and fume the sample to dryness. Add 2 ml of concentrated hydrochloric acid and heat gently. Dilute to 100 ml and boil. Add 1 ml of the lanthanum chloride solution (10 mg La_3O_2) and then add 10 gm oxalic acid. Boil for 10 to 20 minutes. Cool to room temperature and seed with 20 to 30 drops of ammonium hydroxide. Allow to precipitate for at least 4 hours and filter through No. 42 Whatman filter paper. Wash twice with 2% oxalic acid wash solution. Do not wash too often or some thorium will pass into filtrate. Return the paper and precipitate to the original beaker and take to dryness several times with nitric acid. Add 10 ml concentrated nitric acid and 10 ml concentrated perchloric acid. Boil until perchloric acid fumes begin to evolve. Cover with a watch glass and reflux for 5 minutes. Uncover and fume to near dryness. CAUTION: Wear safety glasses.

Dissolve the perchlorates in 50 ml of 10% hydrochloric acid and 5 ml of 5% hydroxylamine hydrochloride. Boil for 5 minutes. Cool to room temperature and transfer to a 250-ml volumetric flask. Add 10 ml of 0.375% Thorin reagent solution and make up to 250 ml volume. Measure the optical density at a wave length of 545 millimicrons on the Beckman "B" spectrophotometer. Determine the micrograms of ThO_2 per 250 ml volume by means of a previously prepared calibration graph. A reagent blank and two standards containing 500 micrograms and 2000 micrograms of ThO_2 should be carried along through the complete procedure with the samples.

CALCULATIONS

$$\% \, ThO_2 = \frac{\gamma \, ThO_2 \text{ per 250 ml (from graph)}}{1{,}000{,}000} \times \frac{100}{\text{sample wt.}}$$

If the sample gives approximately the same reading as the blank, the amount of thorium should be reported as less than the minimum amount detectable (an actual figure based on the sample weight and volumes used) rather than using the term "not detected". The minimum amount detectable may be considered as 100 micrograms per 250 ml volume for colorimetric reading using 1-cm cells and the figure to report may be calculated on this basis, i.e.

$$\% \, ThO_2 = \text{less than } \frac{100}{1{,}000{,}000} \times \frac{100}{\text{sample wt.}}$$

References

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The Volumetric Determination of Thorium

METHOD Th-3

SCOPE

This procedure is designed for thorium determination on high-grade thorium products. Analysis for thorium on low-grade thorium material should be carried out colorimetrically using Thorin reagent (1).

RANGE

Thorium determinations on ore concentrates and thorium products containing greater than 10% or gm/l thorium oxide.

OUTLINE

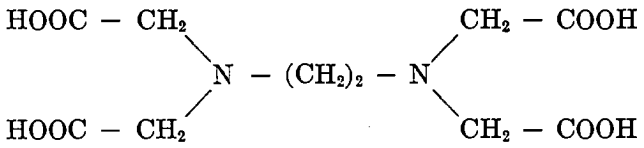
Thorium is separated from most contaminants by means of an oxalate separation. After dissolution of the oxalates, thorium is determined by a spectrophotometric titration using ethylene-diamine-tetraacetic acid (EDTA) as the titrant and pyrocatechol violet as the indicator.

The oxalate separation of thorium is a classical one and has received the attention of many investigators (2, 3, 4, 5, 6). Although there is no separation from the rare earths, this procedure provides an efficient separation from most contaminants, including those which would interfere in the subsequent titration. Conflicting information is prevalent concerning the completeness of precipitation, but it has been found here that, if care is taken, recovery of large amounts of thorium is approximately quantitative (7). It is desirable, however, particularly when high accuracy is required, to carry standards along with a series of samples in order to verify that recovery is quantitative.

Final titration of thorium is carried out with a solution of the chelating compound, ethylene-diamine-tetraacetic acid (EDTA), using the metal sensitive indicator, pyrocatechol violet.

The titration is based on the fact that the coloured complex formed by thorium with pyrocatechol violet is much less stable than the complex formed with the chelating agent, EDTA. Thus, at the equivalence point, the coloured metal indicator complex disappears due to the fact that the thorium is wholly bound by the EDTA. This results in the formation of the colour characteristic of the free indicator at the pH of the titration medium.

The reaction between ethylene-diamine-tetraacetic acid, structural formula



and the metal ion may be represented as follows (8):

$$M^{+n} + Y^{-4} \rightleftharpoons MY^{n-4},$$

where M^{+n} represents the metal ion,

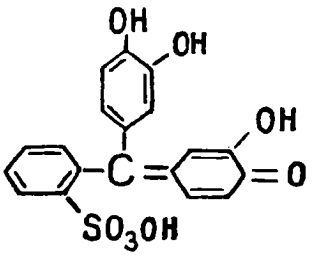
Y^{-4} represents the EDTA ion,

and MY^{n-4} represents the complex.

The complexes forming under ordinary conditions are 1:1 complexes, i.e. one mole of chelating agent per mole of cation.

As EDTA forms complexes with nearly all di-, ter-, and quadrivalent metal ions (8, 9), it is necessary to employ certain techniques to improve the selectivity. Three techniques which may be mentioned are: (a) choice of a pH at which only the ion being titrated reacts with the chelating agent, (b) use of masking agents (added substances forming complexes of much higher stability with interfering ions than those with EDTA), which do not affect the ion being titrated, (c) use of selective separation procedures to eliminate the interfering ion from the solution titrated. In the procedure described here, techniques (a) (pH 2.8 to 3.2) and (c) (oxalate separation), are employed. Because of the liberation of hydrogen ions during the titration, it is helpful to aid pH control by use of a buffer solution.

Of the number of metal indicators available (10), pyrocatechol violet was chosen as the most suitable. This indicator, which may be called pyrocatechol sulfonphthalein or 3, 3′, 4′–trihydroxyfuchsone–2″–sulfonic acid, has the formula



At particular pH values, this compound forms intensely coloured complexes with many metals (10). Ter- and quadrivalent cations form complexes with the indicator in both alkaline and acidic solution, with bivalent cations usually forming complexes only in alkaline solutions. More detailed information on the complexes formed between metal and EDTA, and metal and indicator, can be found in the references (8, 9, 10).

In order to improve the reproducibility of the end-point, the technique of spectrophotometric titration (11, 12, 13, 14) is employed. This technique is of particular value in cases where visual end-points would be obscured and considerable precision is required. Visual end-points are usually indistinct in cases where: (a) the solution is highly coloured and a chemical indicator would be obscured, (b) satisfactory indicators are unavailable, or (c) equilibrium conditions are unsatisfactory (14).

In a spectrophotometric titration, the absorbance is directly proportional to the concentration of the substance being titrated. The end-point is determined by the intersection of two straight lines whose slopes are determined by a number of points.

As a point taken near the equivalence point is no more valid than any other point, deviations in linearity near the end-point do not obscure the true

end-points. For this reason titrimetric analysis may be extended to certain reactions which are not complete at the equivalence point (12, 14).

Because the end-point in the titration of thorium with EDTA using pyrocatechol violet is not particularly sharp, an advantage in sensitivity and precision may be gained by using a spectrophotometric rather than a visual titration procedure. To obtain an adequate slope for the absorbance change at the end-point, at least 1 mg of indicator for each 10 mg ThO_2 has been found necessary.

Removal of Impurities

A number of cations and anions interfere with the titration (10, 15). Cations which form a complex with EDTA of sufficient strength at the selected pH to interfere, include Fe^{+3}, Zr^{+4}, Bi^{+3}, Ti^{+4}, Sn^{+4}, Sb^{+3}, MoO_4^{-2} and WO_4^{-2}. Among the anions which interfere are tartrate, citrate, oxalate, fluoride and sulphate.

The titration can be successfully carried out in the presence of reasonable quantities of perchlorate ion. Small to moderate quantities of nitrate and chloride ions can be tolerated (7). The use of an oxalate separation successfully eliminates a number of commonly-occurring interfering ions including titanium (IV), which, even in small quantities, obscures the end-point and should be completely removed (7). Any small amount of ferric iron remaining after an oxalate separation will affect the end-point, but when reduced to the ferrous form with hydroxylamine hydrochloride and ascorbic acid, iron does not interfere. Hydroxylamine alone does not appear to completely reduce the iron but the addition of a little ascorbic acid completes the reduction. Ascorbic acid alone will reduce the iron but the end-point is sharper if hydroxylamine is present (7). No interference has been found from the presence of appreciable quantities of such rare earths as lanthanum, neodymium and cerium (III), nor with large amounts of uranium (7). No interference may be expected from Pb^{+2}, Ag^{+}, Cd^{+2}, Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Al^{+3}, Zn^{+2}, Ca^{+2}, Mg^{+2}, Ba^{+2}, Sr^{+2}, Na^{+}, K^{+} and NH_4^{+}(10, 15).

APPARATUS

Beakers, Griffin low-form:	250 ml size.
Pipettes, volumetric:	various sizes.
Spectrophotometer, Beckman DU:	(with 1 cm cell compartment, No. 2360 water-cooling light housing cooled directly by tap water). The Bausch and Lomb Cat. No. 33-29-25 Monochromatic Colorimeter (Figure 1) may also be used.
Cells, spectrophotometric:	1 cm size.
Cell holder:	(to hold at least 2 cells).
Nitrogen cylinder:	
Burettes:	10 ml (micro) and 25 ml.
Titration cell:	Join a suitable test tube (1.3 cm dia., 4-8 cm long) to the bottom of a 200 ml electrolytic beaker (5 cm diameter, 11 cm long), and then join a Pyrex 1 cm cell of optical glass to the bottom of the test tube. Cover the beaker and test tube portions with a suitable covering (i.e. black paint) until it is light proof (*see* Figure 2). Cut a suitable hole in a rectangular piece of felt (long enough to cover the cell compartment) and place the cell through the hole. The cell may now be set against a blank by placing it in the regular cell holder.
pH meter:	Beckman, Model G.
Safety goggles:	

REAGENTS

Nitric acid:

Nitric acid, dil.: 1:1 (v/v).

Perchloric acid:

Hydrochloric acid:

Oxalic acid, reagent grade:

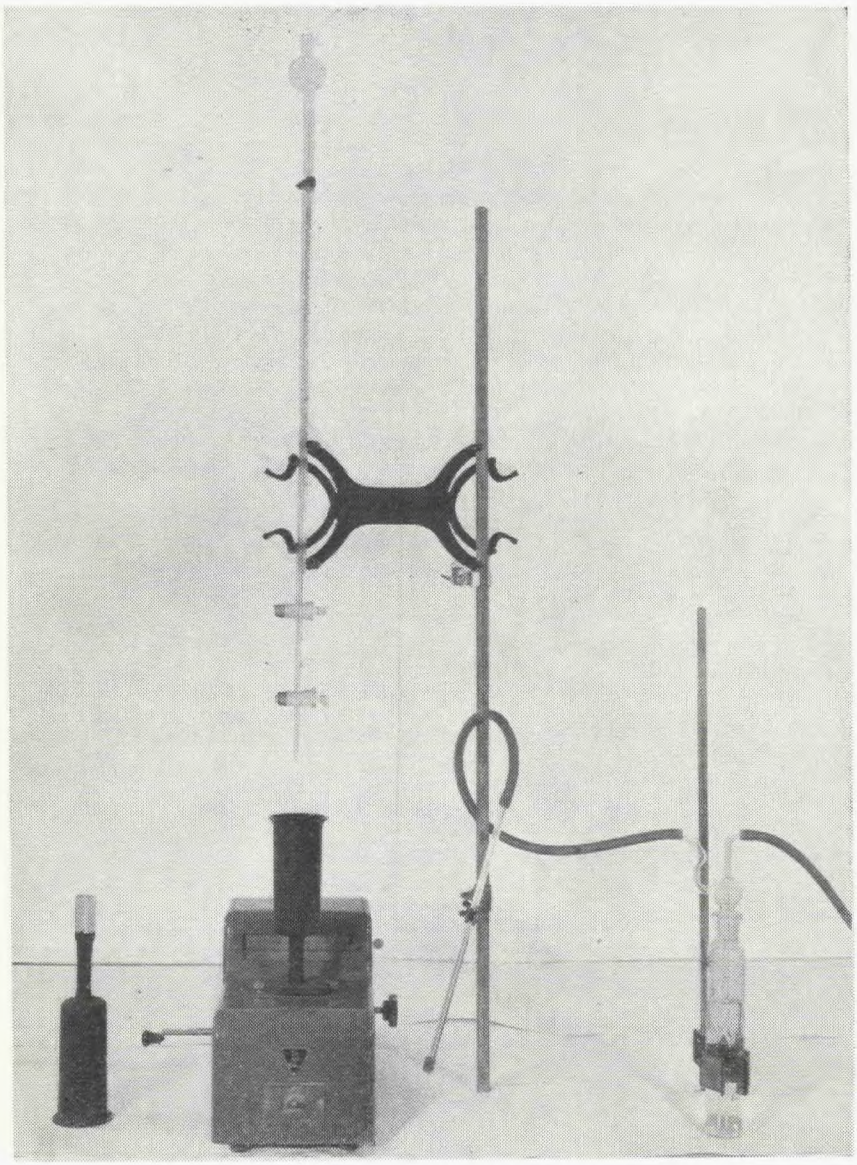


FIG. 1—SPECTROPHOTOMETRIC TITRATION APPARATUS. (WITH BAUSCH AND LOMB COLORIMETER.)

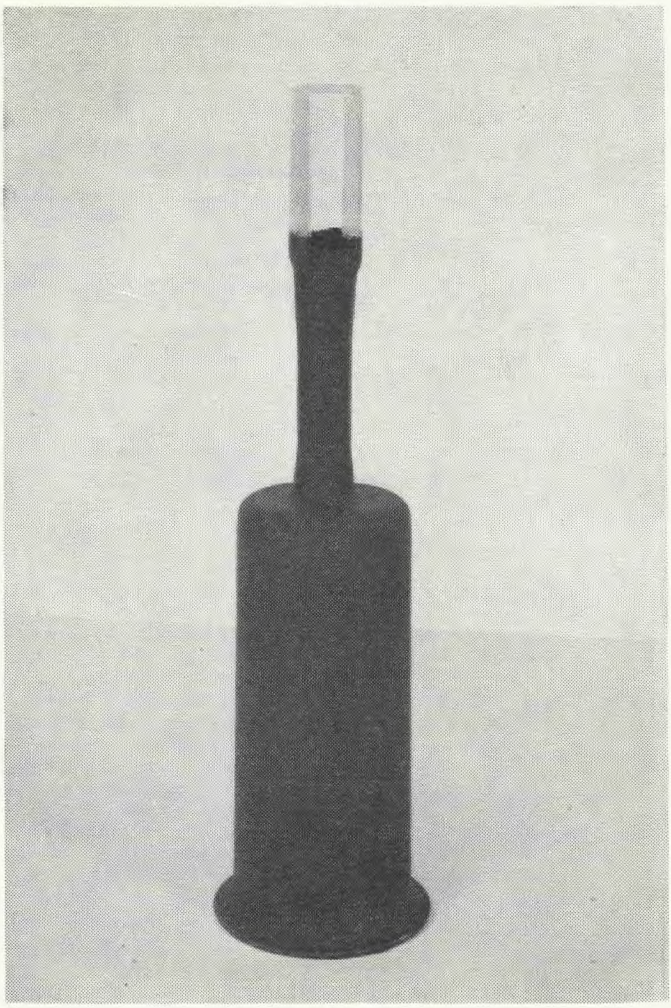


FIG. 2—TITRATION CELL

Oxalic acid, 2%: Dissolve 20 gm of oxalic acid in 1000 ml of distilled water containing 2.0 ml concentrated hydrochloric acid.

Ascorbic acid, 0.5%: Dissolve 0.5 gm of ascorbic acid, reagent grade, in distilled water and dilute to 100 ml.

Hydroxylamine hydrochloride, 5%: Dissolve 5.0 gm of hydroxylamine hydrochloride in distilled water and dilute to 100 ml.

Pyrocatechol violet, 0.1%: (J. T. Baker Chemical Co., Phillipsburg, N.J., Delta Chemical Works, Inc., 23 W. 60th St. New York 23, N.Y.)
Dissolve 10 mg of pyrocatechol violet in 10 ml of distilled water. Prepare the solution fresh daily.

Hydrofluoric acid 1:40: Add 10 ml of 40% hydrofluoric acid to 390 ml of distilled water and mix. Store in plastic bottles.

Sodium acetate, 10%: Dissolve 10 gm of reagent grade in distilled water and dilute to 100 ml.

Hydrochloric acid solution, 1.0N: Add 83.3 ml of concentrated hydrochloric acid to distilled water, and dilute to 1000 ml with distilled water.

Standard thorium solution, 1 ml = 10 mg ThO_2: Dissolve 10 gm of pure thorium oxide (Lindsay Chemical Co.) by heating in a 250 ml beaker with 50 ml concentrated nitric acid, adding dropwise 4-5 drops of 1:40 HF from time to time until the solution is clear. Add 10 ml of concentrated perchloric acid and evaporate to fumes twice, washing down the sides each time with distilled water. Finally evaporate to dryness and take up with a few ml of perchloric acid and distilled water. Dilute to 1000 ml. One ml is equivalent to approx. 10 mg ThO_2.

Standardize by oxalate precipitation, taking at least 50 ml aliquots and igniting the precipitate at 1000° C. If it is necessary to use smaller aliquots, use ammonia precipitation with fresh ammonium hydroxide.

Standard disodium dihydrogen ethylenediaminetetraacetate, 0.010M: Dissolve 7.44 gm of the salt in distilled water and dilute to 1000 ml. Obtain the thorium titer of the solution by titrating against pure thorium solution (1 ml is equivalent to approx. 2.6 mg of ThO_2).

Determination of the thorium factor of the EDTA solution: Pipette suitable aliquots of the standard thorium solution containing 30, 40 and 50 mg ThO_2 into 250 ml beakers. Add 1 ml of 1N hydrochloric acid solution and 0.1 gm of sodium acetate. Then add 1 ml of 5% hydroxylamine solution and boil the solution for 2 minutes. Cool, adjust the pH to 3.05 ± 0.1 by means of dilute ammonia and perchloric acid solution, using a Beckman pH meter, Model G. Add 1 ml of 0.5% ascorbic acid solution. Mix and add 1 ml of 0.1% pyrocatechol violet solution (freshly prepared). Transfer the sample to the spectrophotometric cells and complete the titration as described under Section C of "Procedure". Calculate the thorium factor of the solution as mg ThO_2 per ml of standard solution. Use this figure to verify that adequate recovery is obtained. Use the factor obtained with standards carried through the procedure for calculation of sample results.

PROCEDURE

A. *Dissolution of Sample*

Dissolve 1 gm of the thorium concentrate in 25 ml concentrated nitric acid. If insoluble material remains after boiling with nitric acid for 15-20 minutes, add dropwise 4-5 drops of 1:40 hydrofluoric acid and boil the solution again. Repeat the addition of the dilute hydrofluoric solution two or three times more, heating the solution after each addition for 10 minutes. Add 5 ml of concentrated perchloric acid and take the sample to perchloric fumes. Take up the sample by adding distilled water and dilute to an appropriate volume. Aliquot solution samples directly.

B. *Oxalate Precipitation*

Take a suitable aliquot for the oxalate precipitation and subsequent titration (Table 1). In general make an attempt to take between 20 mg and 60 mg thorium oxide. Amounts larger than this tend to give a somewhat less sharp end-point in the titration. Take the chosen aliquot to dryness on the hot plate, and dissolve the salts with 4 ml of concentrated hydrochloric acid, bringing the volume up to 100 ml with distilled water. Bring the clear solution to a boil. Add 5 gm of oxalic acid and stir thoroughly. Boil the sample for about 20 minutes with intermittent stirring. Cool and allow to stand for at least 4 hours, but preferably overnight.

Filter the precipitate on No. 42 filter paper (Whatman) and wash five or six times with 2% oxalic acid solution containing 0.2% hydrochloric acid. Wash the precipitate from the paper into the original beaker and dissolve the remaining thorium oxalate from the paper by washing the paper with hot 1:1 nitric acid. Evaporate the solution to about 10 ml, add 5-7 ml of concentrated nitric acid and 2-3 ml of concentrated perchloric acid. Evaporate to dryness, making sure all the organic matter is destroyed by adding concentrated nitric acid dropwise to the hot concentrated perchloric acid (and keeping the beaker covered). CAUTION: WEAR SAFETY GOGGLES. Finally fume to dryness. Add 0.25 to 0.50 ml of concentrated perchloric acid and dilute to about 40 ml. Warm until the solution is clear.

C. *Spectrophotometric Titration*

Add 1 ml of 1N hydrochloric acid and then 0.1 gm sodium acetate. Then add 1 ml of 5% hydroxylamine solution, boiling the solution for 2 minutes. Cool and adjust the pH to 3.05± 0.1 by means of dilute ammonia and perchloric acid solutions, using a Beckman pH meter, Model G. Add 1 ml of 0.5% ascorbic acid solution. Mix thoroughly and add 1 ml of 0.1% pyrocatechol violet solution (freshly prepared) for every 10 mg ThO_2 believed present. Transfer the sample to the spectrophotometric titration cell, rinsing the beaker with distilled water. Warm up the spectrophotometer for about 15 minutes, set the wave length scale at 635 mμ and take the absorbance reading against a 1-cm cell containing water or a reagent blank, which has been set at zero absorbance. Stir the solution by bubbling in nitrogen from a nitrogen cylinder, using a movable glass tube with a small piece of tygon tubing on the end to prevent marking the cell. Leave the tube in the titration cell but move it out of the light path and shut off the nitrogen when taking absorbance readings. Add EDTA from a burette in increments, mixing for about 1 minute and taking the absorbance readings, after each addition. The increments may be large (1-3 ml) at first, but as the end-point approaches the colour diminishes more rapidly and small (0.2 ml) increments should be used. When there is no (or a very small) further change in absorbance reading for several additions of EDTA, stop titrating. The colour change is from blue to yellow. Plot absorbance readings as ordinates, against ml of EDTA solution as abscissae (Figure 3). Set the instrument at zero with the water cell before each reading, the cell compartment being covered with a covering of felt as described under "Apparatus". If exterior light conditions are extremely variable, cover the top of the titration cell with a second piece of felt when taking readings. Join the points on the graph to give two straight lines, the points just prior to the end-point forming one straight line disposed at an angle to the abscissae, and those following the end-point forming a second straight line nearly parallel to the abscissae. The intersection of these two lines is the end-point. Note and record the volume of titrant that corresponds to this point, and from this, calculate the thorium content, using the factor obtained in the next section.

D. *Standardization*

Carry aliquots of the standard thorium solution through the procedure and determine a thorium factor for the standard EDTA solution as mg ThO_2 per ml. For example, carry aliquots containing 30, 40 and 50 mg ThO_2 through the

procedure. If the titrations were 11.65, 15.50 and 19.50 ml respectively, the corresponding factors are

$$\frac{30.0}{11.65} = 2.575, \quad \frac{40.0}{15.50} = 2.581, \quad \text{and } \frac{50.0}{19.50} = 2.564.$$

If they agree, average them and use this factor in the subsequent calculation.

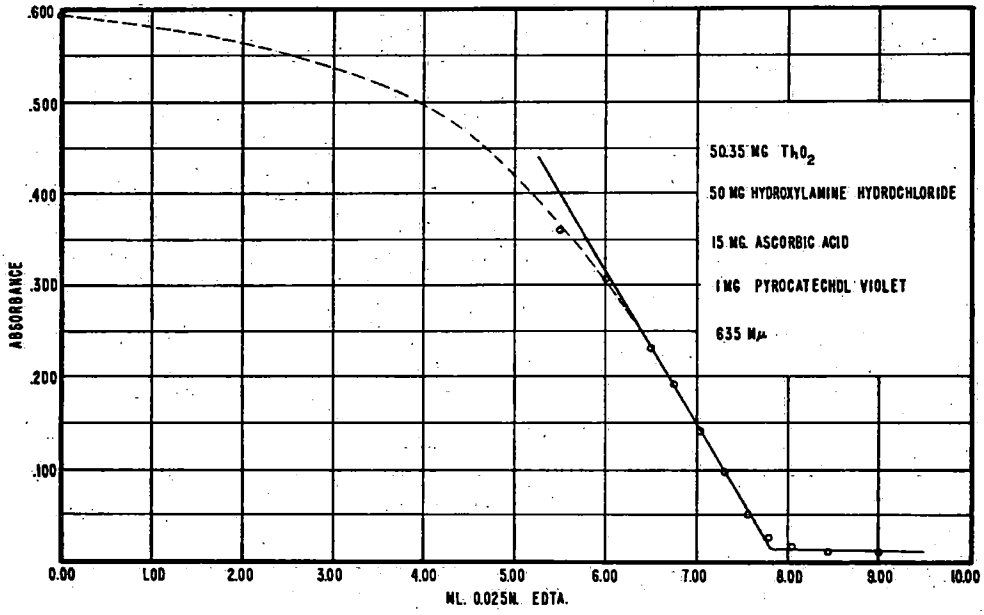


FIG.3 – TYPICAL TITRATION CURVE, SPECTROPHOTOMETRIC TITRATION OF THORIUM WITH EDTA.

Table 1

Suggested Sample Weights and Dilutions

Range %	Sample taken gm	Dilute to ml	Take aliquot ml	Thorium in aliquot for titration mg ThO_2	EDTA required (approx.) 0.025N ml	0.010N ml	0.0025N ml
>90	1.0	100	5	>45 <50	>7 <8	>17.5 <20	—
70	1.0	100	5	35	5.5	14.	—
50	1.0	100	10 or 5	50 25	8. —	20. 10.	—
30	1.0	100	10 or 5	30 15	5. —	12. 6.	— 24.
10	1.0	100	10 or 5	10 5	— —	4. —	16. 8
gm/l	ml						
50	10	100	10	50	8.	20.	—
30	10	100	10	30	5.	12.	—
10	2	—	—	20	—	8.	—

CALCULATIONS

$$\% \ ThO_2 = \frac{T.f}{1000} \times \frac{\text{final dilution}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt., gm}}$$

$$\text{gm/l } ThO_2 = \frac{T.f}{1000} \times \frac{\text{final dilution}}{\text{aliquot taken}} \times \frac{1000}{\text{sample volume}}$$

where T = titration volume, ml. of standard EDTA solution, taken from titration graph.

f = the thorium factor of the standard EDTA solution, mg ThO_2 per ml.

If no titration is obtained do not report "not detected" since the method as outlined is relatively insensitive. Instead determine the thorium content by one of the procedures given in METHOD Th-1, or report the result as "less than" the lower limit of detection, an actual figure based on the sample weight or volume used. The lower limit for this method may be taken as 3 mg ThO_2 and the figure to report should be calculated on this basis.

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PART III

Supplementary Methods

Contents

PART III—SUPPLEMENTARY METHODS

Contents—Continued

Contents—Continued

Contents—Concluded

A
and
B

The Determination of "Acid-Insoluble" or Impure Silica in Ores and Mill Products

METHOD A.I.-1

SCOPE

The methods given below are applicable to all ores and mill products.

RANGE

The method is suitable for acid insoluble in the range between 0.1 to 100%.

OUTLINE

The acid insoluble is the residue which remains after the ore or mill products have been treated with acids. It is often referred to as impure silica and usually consists mainly of silica and undecomposed silicates. It may also include phosphates of zirconium, titanium, thorium, iron, tin, etc., sulphates of barium or lead, chlorides of silver and lead, and acids such as tungstic, stannic, vanadic, niobic, antimonic, etc., if the above elements are present in the ore. Fluorine, if present, causes low results since some of the silica will be volatilized as silicon tetrafluoride. The acid insoluble is determined by digesting the ore or mill products with appropriate acids and evaporating the solution to dryness. The baked residue is digested with weak acid, filtered, and the residue ignited and weighed. If fluorine and fluorides are absent the true silica may be found by treating the weighed acid insoluble with hydrofluoric and sulphuric acids.

REAGENTS

Nitric acid concentrated:

Hydrochloric acid, concentrated and 1:1:

Ammonium chloride:

PROCEDURE

For Ores and Solids

1. *For Sulphide and Lead Ores*

Weigh a portion of the sample into a 250-ml beaker. Add 10 ml of water and 10 ml of concentrated nitric acid. Heat gently until strong action ceases and evaporate just to dryness. Wash down the sides of the beaker with distilled water, add 5 ml of concentrated hydrochloric acid, boil, evaporate to dryness and bake for 1-2 hours at 110°C. Cool, add 30 ml of 1:1 hydrochloric acid, add a few drops of hydrogen peroxide and heat to boiling. Cool slightly, add 1-2 gm of ammonium chloride and 10-15 ml of distilled water. Heat and filter through a No. 42 Whatman paper, using filter pulp if necessary. Wash the residue a few times

with hot 1:1 hydrochloric acid, then with hot 5% ammonium chloride solution and finally with hot water. If the ore is high in silver or tungsten, rewash the washed residue with hot dilute ammonium hydroxide and then with hot water. Transfer the paper and residue to a weighed crucible, add 4 or 5 drops of 1:1 sulphuric acid, dry, carefully char and burn off the carbon. Ignite at about 900°-1000° C, cool in a desiccator and weigh.

2. *Oxidized Ores, Roasted Ores, etc.*

Weigh a portion of the sample into a 250-ml beaker. Add 10-15 ml of 1:1 hydrochloric and 5 ml of hydrobromic acid, boil and evaporate nearly to dryness. Cautiously add 1-2 ml of nitric acid and 5 ml of hydrochloric acid. Evaporate to dryness and bake for 1-2 hours at about 110°C. Cool, add 30 ml of 1:1 hydrochloric acid, and a few drops of hydrogen peroxide. Heat to boiling and continue as for sulphide ores.

If fluorine is absent silica may be determined in the above residue by repeated treatment of the residue with a mixture of hydrofluoric and sulphuric acid until a constant weight is obtained. If silica is to be determined in the residue all ignitions and weighings should be carried out in a platinum crucible.

CALCULATIONS

$$\% \text{ Acid Insoluble} = \frac{\text{wt. residue (gm)} \times 100}{\text{sample wt.}}$$

Reference

1. Low, A. H., Weinig, A. J., and Schoder, W. P.: Technical Methods of Ore Analysis, 11th ed., New York, John Wiley and Sons, 1939.

The Fluorimetric Determination of Aluminum with 8-Hydroxyquinoline

METHOD Al-1

SCOPE

This method is intended for the rapid, accurate determination of aluminum in ores, mill products and solutions.

RANGE

The method is extremely sensitive and will detect as little as 0.0005% or gm. of aluminum per litre. The actual range corresponds to 0.5 to 50γ aluminum in the final 2-ml aqueous aliquot taken for extraction (i.e. 0.5 to 50γ in the 25 ml chloroform extract) (1).

OUTLINE

Aluminum forms a complex with 8-hydroxyquinoline which is extracted by chloroform at pH 4.6 (2, 3). The resultant solution, when illuminated with ultra-violet light (365 mμ), fluoresces brilliantly with a greenish yellow colour over the wave lengths 470 to 550 mμ (4). The emitted fluorescence bears a linear relationship to aluminum concentration in the range 0.5 to 50γ per 25 ml of chloroform (1).

Fluoride and phosphate interfere by complexing the aluminum and preventing its extraction. The interference of phosphate is overcome by using an excess of 8-hydroxyquinoline, but fluoride must be removed. This is accomplished by a preliminary fuming with perchloric and sulphuric acids (5).

Uranium, iron, manganese, vanadium, titanium, zirconium, chromium, antimony, cobalt, copper and nickel are extracted by 8-hydroxyquinoline under the condition employed. Of these, iron, manganese (1), vanadium and titanium (6) quench the fluorescence; and chromium (1), zirconium (7) and uranium enhance it. The enhancement due to uranium is slight (0.5 mg $\doteq$ 0.4 μg Al) under our conditions. Chromium is removed as chromyl chloride in the preliminary fuming (8). If large amounts are present, reduction with ferrous sulphate permits its removal in the sodium hydroxide precipitate. Uranium, iron, manganese, zirconium and titanium (in the presence of added iron if necessary) (9), are removed by sodium hydroxide precipitation. In the case of samples containing large amounts of magnesium or nickel, however, aluminum is carried down and lost in the precipitate. Magnesium does not interfere if the concentration is not greater than the aluminum concentration, but 10 mg of magnesium will co-precipitate half of a 1-mg portion of aluminum. If large amounts of magnesium are present, a prior separation of aluminum with ammonium hydroxide in the presence of ammonium chloride, using ferric iron as a carrier, may

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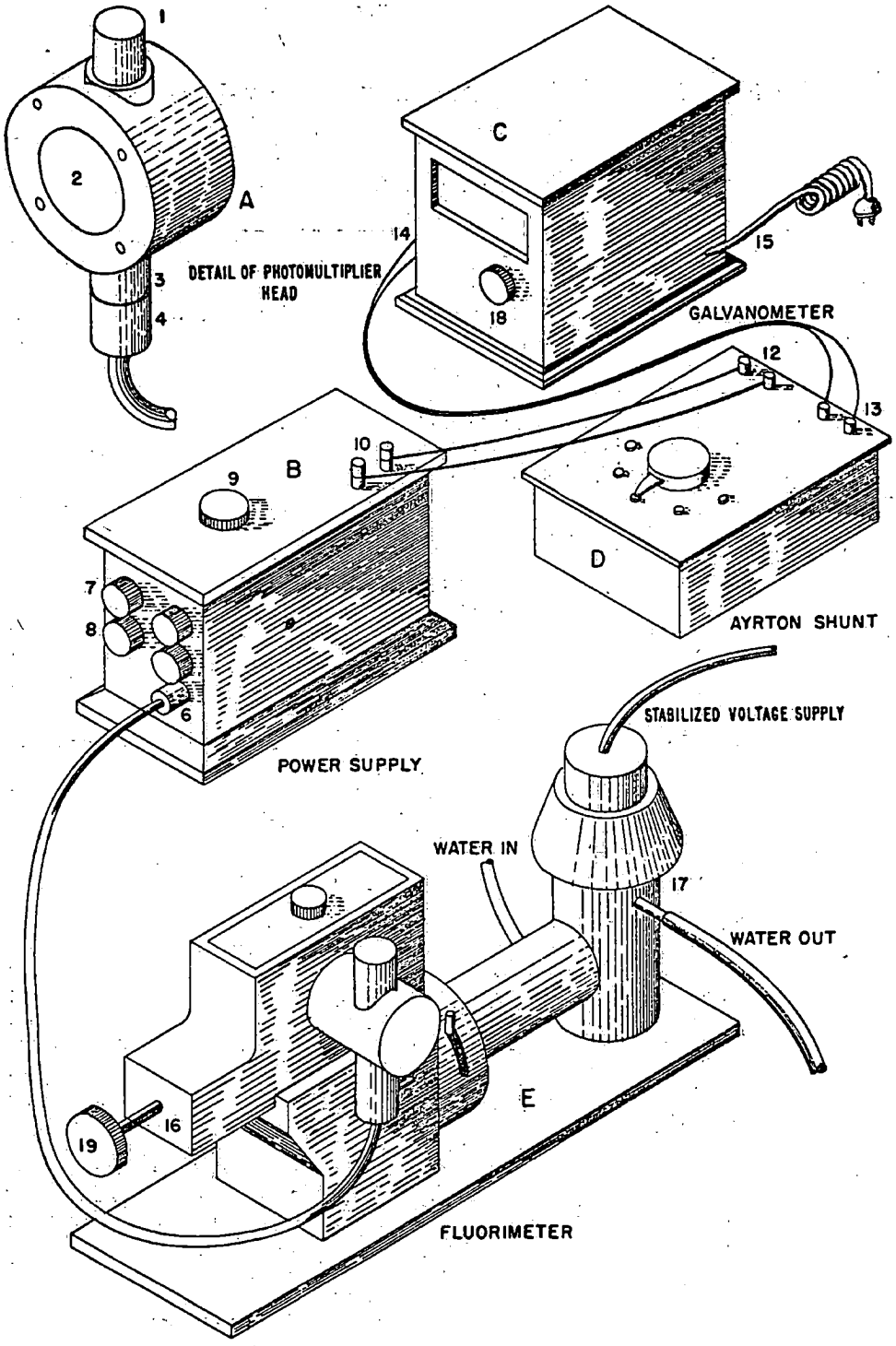

Fig. 1 FLUORIMETER-PHOTOMULTIPLIER ASSEMBLY.

be necessary (14). Titanium and vanadium can also be removed by cupferron extraction from dilute acid solution (10) but this has not been found necessary to date and is not included in the method.

Gallium, whose 8-hydroxyquinolinate also fluoresces, resembles aluminum in properties and would be included by this method. It could be removed by prior extraction of the 8-hydroxyquinolinate at pH 2.6 (11), or its interference greatly decreased by suitable choice of filter for the fluorescent emission (4). Its occurrence is so infrequent that these precautions are not considered necessary.

APPARATUS

pH Meter:	Beckman Model H-2 (see Instruction Bulletin)
Separatory funnels:	60 ml Squibb pear-shaped
Burettes:	two 100 ml size
Volumetric flasks:	100 and 500 ml
Pipettes:	2, 5, 10, 25, 50 ml sizes.
Erlenmeyer flasks:	100 ml.
Fluorimeter—Photomultiplier Assembly (Figure 1):	A General Electric Model H-100 A4 lamp (stabilized by a Sola constant-wattage 100 watt transformer Cat. No. 301883) in a water cooled housing (17), illuminates the solutions, contained in cells in a Beckman Fluorescence Attachment (Beckman Cat. No. 2980) through a filter which isolates the 3650 Å mercury line. Fluorescent light, passed through a yellow filter to remove stray ultra violet light, is picked up by a Farrand Electron Multiplier Photometer (Cat. No. 83643/1) consisting of a detector unit (Cat. No. 83104) (A), containing a 1 P 21 photomultiplier tube (Cat. No. 76231), a battery power supply and control unit (Cat. No. 86109) (B), connecting cable (Cat. No. 86108), a Leeds and Northrup 10,000 ohm Ayrton shunt with factors of 1, 0.1, 0.01, 0.001, 0.0001, 0 and Infinity (L. and N. Cat. No. 2166) (D), and a spotlight galvanometer (Farrand Cat. No. 85653) (C). Further information on the photomultiplier unit may be found in the manufacturer's literature (12, 13).
Batteries:	The batteries employed in the power supply must be replaced regularly. The types and numbers of batteries required are: Burgess U20 or Eveready 413E (30 volts): 27 required. Burgess K20 or Eveready 430E (30 volts): 3 required. Burgess 2FBP or Eveready flashlight (1½ volts): 1 required.
Fluorimeter cells, Corex, 1 cm:	with transparent bases, matched set of four, e.g. Fisher 14-383-135.

NOTE: A line-operated instrument, e.g. Klett Model 2070, will be found less expensive to operate if the determination is employed infrequently, athough it may be less precise than the instrument described.

REAGENTS

8-hydroxyquinoline solution:	Dissolve 15 gm of 8-hydroxyquinoline in 1 litre of 2M acetic acid.
Standard aluminum solution:	Dissolve 0.0478 gm potassium alum $AlK(SO_4)_2$ in 1 litre of aluminum-free distilled water, 1 ml = 5γ Al.
Buffer:	Mix equal volumes of 2M acetic acid (12 gm CH_3COOH per 100 ml of solution) and 2M ammonium acetate (15.4 gm CH_3COONH_4 per 100 ml of solution).

Distilled water:	If blank is high, the water must be redistilled or de-ionized in aluminum-free apparatus.
Ferrous sulphate, 15%:	15 gm $FeSO_4.7H_2O$ in 100 ml water.
Chloroform:	Reagent grade, redistilled if necessary.
Calcium sulphate:	$CaSO_4$. reagent grade.
Sodium hydroxide:	30% c.p. sodium hydroxide.
Sulphuric acid:	10% v/v, for pH adjustment.
Ammonium hydroxide:	10 v/v for pH adjustment.
Sulphuric acid:	1:1 v/v.
Hydrochloric acid, concentrated:	reagent grade.
Nitric acid, concentrated:	reagent grade.

PROCEDURE

A. Preliminary Treatment

1. *Solid Samples*

NOTE: Carry a blank of all the reagents through the entire procedure. An alternative method for determining the blank correction is to run a 5γ and a 10γ standard. The blank is then given by 2 (reading of 5γ standard)-(reading of 10γ standard).

Weigh accurately a 0.1- to 2.0-gm sample, depending on the aluminum concentration (Table 1), into a 150-ml beaker. Add 20 ml hydrochloric acid and 5 ml nitric acid. Cover and digest on a hot plate to dissolve. Remove the cover, add 5 ml perchloric acid, and fume to dryness, but do not bake. Add 5 ml of 1:1 sulphuric acid, triturate with a stirring rod and fume again. Add 20-30 ml distilled water and warm to dissolve.*

2. *Solution Samples*

Choose a suitable aliquot based on the estimated aluminum content (Table 1) Evaporate to dryness and take to fumes twice with 5-ml portions of 1:1 sulphuric acid as described above. Add 20-30 ml distilled water and warm to dissolve.*

B. Separations and Development of Fluorescence

Boil the solution so obtained for 10 minutes. Add 10 ml of 30% sodium hydroxide, boil 5 minutes and cool. Transfer to a 500-ml volumetric flask and dilute to the mark (the pH should now be >12). Let stand until the precipitate has settled. Take an aliquot and filter into an appropriate sized volumetric flask (Table 1). Make to volume, mix well, and transfer 25 ml of the second dilution into a 50-ml beaker. Adjust to pH to approximately 3.5 with 1% sulphuric acid using a pH meter and measuring the acid accurately using a burette since this constitutes a third dilution.

After adjusting the pH, pipette 2 ml into a 60-ml separatory funnel which already contains 1 ml of prepared 8-hydroxyquinoline reagent. Add 3 ml of buffer solution, 15 ml of distilled water and 25 ml of chloroform. The order of addition is important and must be strictly adhered to. All volumes must be carefully measured and the total volume in the separatory funnel should be 46 ml.

Into a second separatory funnel, pipette 2 ml of the standard aluminum solution (10γ Al) and the same volumes of reagents as noted above.

Shake the samples and standard 10 seconds each and let the layers separate. Run off the chloroform into a 100-ml Erlenmeyer flask containing approximately

* If much chromium or titanium is present, add 10 ml of 15% ferrous sulphate solution at this point.

1 gm of calcium sulphate ($CaSO_4$) to remove any water carried down with the chloroform. Decant the chloroform into a 1-cm cell and compare its fluorescence with that of the 10γ standard.

Fluorimeter Operation

Turn on the water supply to the lamp-housing (17 in Figure 1) of the fluorimeter (E). Make sure that the photomultiplier shutter (1) is closed. Turn on the ultraviolet lamp, check to make sure it lights, and leave it on 15 minutes to ensure stable operation. Set the Ayrton shunt (D) at "position 1". Plug in the galvanometer plug (15) and zero the galvanometer (C) by means of the knob (18) on the front of its case.

Dark Current Adjustment

Turn the sensitivity coarse and fine knobs (8) on the photomultiplier power supply (B) fully clockwise. Press the zero button (9), and adjust the dark current coarse and fine knobs (7) on the power supply (B) until the galvanometer spot stays in the same position whether the zero button (9) is pressed or not.

Finally turn the sensitivity knobs back fully counter-clockwise and adjust the knob (18) on the galvanometer, to zero the galvanometer spot again. Check this adjustment at intervals if necessary, but do not disturb it otherwise.

Scale Adjustment and Sample Reading

Put the blank, the standard (consisting of 10γ Al in the final 25 ml chloroform extract) and the samples each in a separate Beckman 1-cm Corex fluorimeter cell, and insert the cells in the holder. Place the holder in the fluorimeter (E) and replace the cover. By means of the knob (19) on the front of the fluorimeter (E), move the blank into the light path. Open the photomultiplier shutter (1). With the Ayrton shunt (D) set at 0.1 adjust the sensitivity knob (8) on the photomultiplier power supply (B), so that the galvanometer (C) reads 15 to 30.

NOTE: The galvanometer scale is 10 cm in length graduated in millimeters, and the actual reading is the galvanometer reading in cm. taken to the nearest 0.05 cm, divided by the shunt setting.

Move the standard into the light path, adjust the Ayrton shunt so that the spot appears on the galvanometer scale (normal shunt setting 0.01 giving a reading of 600–800) and again note the reading. Check the blank setting again after reading the sample.

Repeat this procedure with the two samples. If more than two samples are being read, close the photomultiplier shutter, remove the cell holder, take out the two sample cells and empty them. Rinse with chloroform, then rinse several times with the next samples, and refill with these samples. Replace the cells in the holder, put the holder in the fluorimeter.

Replace the cover, open the photomultiplier shutter and repeat the operations as before.

Determine the number of micrograms of aluminum in the 2-ml aliquot taken for analysis as follows: Subtract the blank reading from the sample reading, divide by the reading for 10γ Al, i.e.

$$\frac{\text{Sample Reading—Blank Reading}}{\text{Standard (10}\gamma\text{ Al) Reading—Blank Reading}} \times 10 = \gamma \text{ Aluminum in original 2-ml aliquot}$$

Table 1

Recommended Aliquots and Dilutions for Solution Samples

Estimated Range gm/l	1st Dilution ml	2nd Dilution ml	3rd Dilution ml	Final Dilution ml
0.05	25/500	—	25/(25 +t)*	2
0.1	25/500	50/100	25/(25 +t)*	2
0.2	10/500	50/100	25/(25 +t)*	2
0.5	5/500	50/100	25/(25 +t)*	2
1.	5/500	25/100	25/(25 +t)*	2
2.	5/500	10/100	25/(25 +t)*	2
5.	5/1000	10/100	25/(25 +t)*	2

* t = volume of 1% sulphuric acid required to neutralize the aliquot from the second dilution.

Table 2

Recommended Sample Weights, Aliquots and Dilutions for Solid Samples

Estimated Range %	Sample Weight gm	1st Dilution ml	2nd Dilution ml	3rd Dilution ml	Final Dilution ml
0.05	2.5	500	—	25/(25 + t)*	2
0.1	2.5	500	50/100	25/(25 + t)*	2
0.2	1.0	500	50/100	25/(25 + t)*	2
0.5	0.5	500	50/100	25/(25 + t)*	2
1	0.5	500	25/100	25/(25 + t)*	2
2	0.5	500	10/100	25/(25 + t)*	2
5	0.5	1000	10/100	25/(25 + t)*	2

* t = volume of 1% sulphuric acid required to neutralize the aliquot from the second dilution.

CALCULATIONS

Solid Samples

$$\% \text{ Aluminum} = \frac{\gamma \text{ Aluminum in 2-ml aliq.}}{1{,}000{,}000} \times \frac{\text{1st dil. vol.}}{\text{sample wt.}} \times \frac{\text{2nd dil. vol.}}{\text{aliq. of 1st dil.}} \times \frac{\text{3rd dil. vol.}}{\text{aliquot of 2nd dilution}} \times 100$$

If the sample gives approximately the same reading as the blank, the amount of aluminum shall be reported as less than the minimum detectable (an actual figure based on the sample weight and volumes used) rather than using the term "not detected". The minimum amount detectable may be considered as 0.5 micrograms aluminum in the 2-ml aliquot taken for extraction and the value to report may be calculated on this basis i.e.

$$\% \text{ Al} = \text{less than } \frac{0.5}{1{,}000{,}000} \times \frac{\text{1st dilution volume}}{\text{sample weight}} \times \frac{\text{2nd dilution volume}}{\text{aliquot from 1st dilution}} \times \frac{\text{3rd dilution volume}}{\text{aliquot from 2nd dilution}} \times 100$$

and similarly for solutions.

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The Determination of Arsenic: Distillation-Bromatometric Method

METHOD As–1

SCOPE

The method described here is to be used for the accurate determination of arsenic in the higher ranges, and in those cases where the presence of interfering elements such as copper, iron, antimony, bismuth and chromium in excessive amounts makes the colorimetric method (As–P_2O_5–2) unreliable. In these latter cases it is possible to combine the decomposition and distillation steps from this method with the colorimetric finish from METHOD As–P_2O_5–2 to handle highly impure material containing only small amounts of arsenic.

RANGE

The method will determine arsenic as low as 0.01%, using the weak titrant. If a colorimetric finish is used, it should be possible to determine as little as 0.001%.

OUTLINE

Potassium bromate readily oxidizes trivalent arsenic at room temperature in strong 1.5 to 3.0 N hydrochloric acid solution (1, 2),

$$BrO_3^- + 3\ As^{3+} + 6H^+ \longrightarrow Br^- + 3\ As^{5+} + 3\ H_2O.$$

Trivalent antimony, thallous thallium, and hydrazine, will titrate if present. Cuprous copper and stannous tin, though easily air-oxidized, will also titrate.

The use of Bordeaux as an indicator permits carrying out the titration at room temperature. This indicator, like most of those used for bromate titrations, is of the irreversible type; that is to say, an excess of the titrant destroys the indicator. The destruction of the indicator may be premature to some extent, so that it is well to add a few additional drops of indicator at the end-point to make sure that it has been reached.

Arsenic is separated from various interfering elements by reduction to the arsenious state, using a hydrazine salt and potassium bromide, followed by distillation of the arsenious chloride formed, in the presence of hydrochloric acid. The presence of the potassium bromide is stated to result in a considerable reduction in the time required for complete distillation of the arsenic (3). The boiling point of arsenious chloride is 130.2°C. It begins to volatilize below 108°C and is actively volatile at 120°C (4). It has been found here (5) that a temperature of distillation above 110°C is necessary to ensure complete recovery in 100 ml of distillate. Maintenance of this temperature is only possible if care is taken to avoid too great a dilution of the sample prior to distillation and to avoid suck-back of the distillate during the distillation. Antimony trichloride boils at

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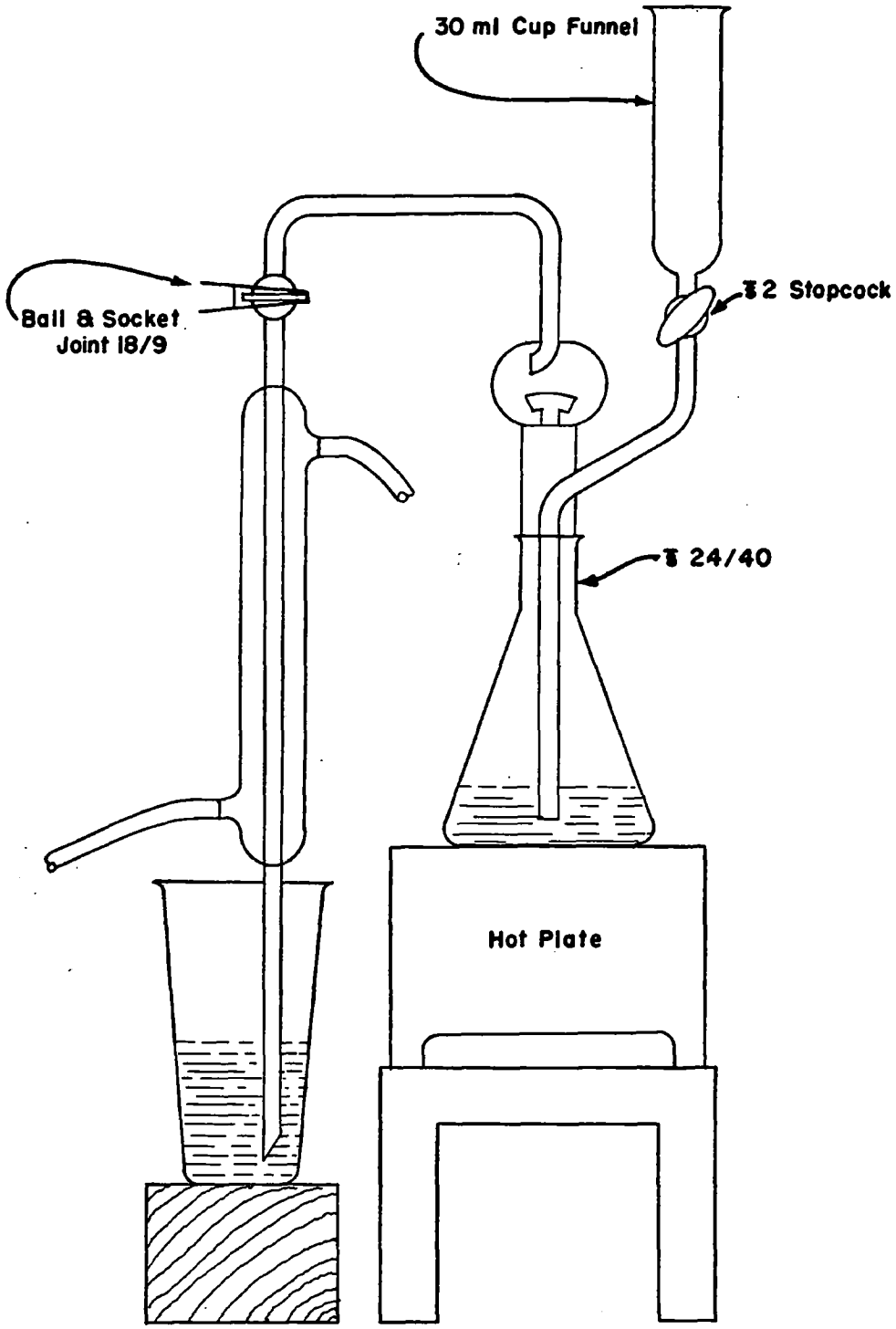

FIG. 1.– ARSENIC DISTILLATION APPARATUS

223.5°C and is not actively volatile below 180°C. Stannic chloride boils at 114°C, but it will ordinarily be reduced to stannous chloride, (b.p. 603°C) in the method outlined here (4).

Care must be taken that the contents of the distillation flask do not go to dryness if hydrazine sulphate is used, since this salt decomposes to give SO_2 which is titrated by the bromate. For this reason the hydrazine dihydrochloride is preferred for the reduction (5).

All-glass apparatus must be used, since it has been found that rubber stoppers take up arsenic when high-arsenic samples are run, and give it up when low-arsenic samples are run (5).

The reduced arsenic can also be titrated using iodine solution if the distillate is first neutralized and an excess of sodium bicarbonate added.

$$As_2O_3 + 2\ H_2O + 2\ I_2 \longrightarrow As_2\ O_5 + 4H\ I.$$

The bicarbonate is necessary to neutralize the hydriodic acid which otherwise accumulates and eventually halts the reaction. Sodium bicarbonate, unlike the soluble alkaline hydroxides and normal carbonates, does not react with iodine. Starch indicator is used and for this reason the iodine titration may be preferred by those who have difficulty in observing the end-point of the bromate titration.

Alternatively, and particularly for samples low in arsenic, the colorimetric finish may be used.

OCCURRENCE

Arsenic occurs in the nickel cobalt arsenides of the Eldorado mine at Port Radium, N.W.T. As a result it is also present, as arsenates, in the leach liquor and in the product from the acid-leach: aluminum reduction process used there. It may occasionally be present, as uranous or uranyl arsenate, in the residue as a result of poor pH control during leaching. Other Canadian ores contain, as a rule, less than 0.01% arsenic. Sulphide ores may contain arsenic, in pyrite or arsenopyrite.

APPARATUS

All-glass distillation apparatus:	*See* Figure 1.
This can also be assembled using:	
Flask, Erlenmeyer, 300 ml, 24/40 joint:	Corning Cat. No. 5000, code 412530.
Connecting tube and funnel, 24/40:	Scientific Glass Co. cat. No. J-1843.
Distilling head, McHargue, 24/40:	Scientific Glass Co. cat. No. J-1147.
Ball joint, 28/15, ball only:	Corning cat. No. 6762, code 418590, to be joined to distilling head.
Condenser, Liebig 25 cm with 28/15 semi-ball socket at top:	Scientific Glass Co. cat. No. SB-640.
Beakers, Berzelius, tall form with spout, 300 ml:	Corning cat. No. 1060, code 420360.
Hot plate, 6 place, low temp:	E. H. Sargent Co. cat. No. 41315.

Steam bath:	
Beakers, Griffin low-form:	250 ml, 400 ml.
Flasks, Erlenmeyer, narrow mouth:	300 ml.
Crucibles, porcelain, Coors:	60 ml size.
Crucibles, nickel:	60 ml size.
Glass beads:	
Beaker tongs:	
Flask tongs:	
Safety glasses:	
Crucible tongs:	
Burettes:	10 ml, 25 ml and 50 ml.

REAGENTS

Nitric acid concentrated:	
Hydrochloric acid, concentrated:	
Hydrochloric acid, dil.:	1:1 v/v.
Sulphuric acid, concentrated:	
Sulphuric acid, dil.:	1:1 v/v.
Sodium carbonate:	
Sodium bicarbonate:	
Potassium nitrate:	
Potassium (or sodium) sulphite:	
Bromine solution:	Dissolve 75 mg potassium bromide and 50 ml bromine in 450 ml water.
Potassium chlorate:	
Ferrous sulphate:	
Hydrazine dihydrochloride (or sulphate):	
Sodium hydroxide solution, 50%:	e.g. B and A Code 2327.
Bordeaux indicator:	0.1 gm Bordeaux (B.C.I. No. 88) in 100 ml water.
Phenolphthalein indicator:	0.1% in alcohol.
Starch solution:	1 gm soluble starch in 100 ml boiling water. Cool and store in a tightly sealed bottle.
Standard potassium bromate solution (regular):	Dry reagent grade potassium bromate at 150°C for 1 hour. Weigh out 3.716 gm, dissolve in water, transfer to a volumetric flask, and make to 1 litre. 1 ml = 0.005 gm As (need not be standardized).
Standard potassium bromate solution (weak):	Dilute 100 ml of the regular solution to 1 litre—1 ml = 0.0005 gm As.
Standard iodine solution, 0.1 N:	Place 20-25 gm KI in a 1-litre flask. Dissolve it in as little water as possible. Add 12.7 gm reagent grade iodine. Shake the flask until all the iodine is dissolved. Dilute to volume. Standardize the solution against arsenious oxide.

Standardization of the standard potassium bromate solution

If the potassium bromate used is of unknown concentration, the solution may be standardized against arsenious oxide.

Weigh out 0.2642 gm of pure As_2O_3 (0.20 gm As), dissolve in 2 ml of N sodium hydroxide solution, then neutralize with 15% v/v hydrochloric acid solution. Transfer to a 400-ml beaker and make up to the volume normally used in titrating the samples, using 15% v/v hydrochloric acid. Add a small crystal of potassium bromide and 4 drops of Bordeaux indicator. Titrate to the disappearance of the pink colour. When the colour begins to fade add 2 drops more of the indicator and continue to titrate slowly to the end-point. Record the titration. The arsenic factor is given by

$$\text{f (gm As per ml solution)} = \frac{\text{wt. } As_2O_3 \text{ taken, gm}}{1.341 \times \text{titration, ml}}$$

The factor for the weak standard bromate solution is given by

$$\text{f (weak bromate)} = \text{f (regular bromate)} \times \frac{\text{aliquot taken}}{\text{final volume}}$$

Standardization of standard iodine solution

Weigh out accurately 0.2-gm portions of pure dry arsenious oxide into 400-ml beakers and dissolve in 2 ml of N sodium hydroxide solution. Add a few drops of phenolphthalein indicator, then add N hydrochloric acid until the solution is just colourless. Add 10 gm of sodium bicarbonate, stir to dissolve, and add 10 ml of starch solution. Titrate with the standard iodine solution to a permanent blue colour. Record the titration. The normality of the solution is given by

$$N = \frac{\text{weight of } As_2O_3 \text{ taken} \times 1000}{\frac{197.82}{4} \times \text{titration, ml}}$$

1 ml N/10 iodine = 0.003746 gm As.

The arsenic factor is calculated directly as

$$\text{f(gm As per ml)} = \frac{\text{wt. } As_2O_3 \text{ taken, gm}}{1.341 \times \text{titration, ml}}$$

PROCEDURE

A. Initial Treatment

1. *Solid Samples*

(a) *General decomposition method.* (*Wear Safety Glasses*)—Weigh a sample of suitable size (Table 1) into a 300-ml Erlenmeyer flask. Add 5-7 gm potassium bisulphate, 5-10 ml of concentrated sulphuric acid and one-eighth of a 9-cm filter paper. Heat the mixture gradually while swirling the flask over the flame of a Meker burner until the carbon is completely oxidized and the solution becomes clear and straw-coloured. *Do not heat to violent fuming.* Cool. Cautiously add 20-50 ml of water and boil to expel any SO_2. Transfer to a 300-ml distillation flask, filtering if there is a large amount of residue. Dilute to 50-75 ml.

(b) *Fusion Method*—Mix a suitable sample (Table 1), 0.5 to 2 gm in weight, with 3 to 5 gm of a 1:1 mixture of sodium carbonate and potassium nitrate in a large porcelain or nickel crucible. Cover with 2-3 gm of the fusion mixture.

Heat the mass gradually using a low flame at the start and taking plenty of time so the mixed salts will melt and permeate the mass before decomposition occurs (to prevent loss of arsenic by volatilization). Finally, heat with the full flame of the burner until decomposition is complete. Prolonged heating over a very hot flame (blast burner) may be necessary, as for example with oxidized ores containing lead. The melt should appear smooth and homogeneous when swirled. Cool, place the crucible in a beaker and digest the melt with hot water until thoroughly disintegrated. Filter into a 300-ml distillation flask and wash with hot water. Add about 1 gm of sodium or potassium sulphite and 5 ml of 1:1 sulphuric acid. Boil to expel the excess SO_2. Let cool and dilute to 50-75 ml.

(c) *Special Method, Pyrites and Arsenopyrites*—Weigh a suitable sample (Table 1) into a 400-ml beaker. Add 10-50 ml bromine solution, cover the beaker and let stand in a warm place for about 20 minutes. Cautiously add 20 to 50 ml of concentrated nitric acid in 5- to 10-ml portions, letting the reaction subside after each addition. Evaporate to dryness on a steam bath or on a hot plate at a low heat, (to prevent spattering and also to avoid volatilization of arsenic pentabromide). Let cool and wash down the sides of the beaker. Add 10-12 ml of 1:1 sulphuric acid and evaporate to strong fumes of SO_3. Cool, wash down the sides of the beaker and evaporate again to strong fumes. Cool and cautiously dilute to 20-50 ml with water. Digest at low heat till only a siliceous residue remains undissolved. Filter into a 300-ml Erlenmeyer distillation flask. Add 1 or 2 gm potassium or sodium sulphite to the filtrate and boil to expel SO_2. Let cool and dilute to 50-75 ml.

(d) *Alternative Method, Pyritic Material*—Weigh a suitable sample (Table 1) into a 400-ml beaker. Add 10 ml of nitric acid and about 0.5 gm of potassium chlorate. Warm to dissolve the chlorate, then evaporate to dryness on the hot plate.

*Add 3 to 5 ml of hydrochloric acid and evaporate to dryness. Add 5 ml more of hydrochloric acid and again take to dryness. Add 20 ml of dilute HCl(1:1 v/v) and heat gently to dissolve the soluble salts. Filter (if necessary) into a 300-ml Erlenmeyer distillation flask. Let cool and dilute to 50-75 ml.

2. *Solution Samples*

Leach Liquors Containing Oxidizing Agents—Aliquot a suitable sample (Table 2) into a 300-ml Erlenmeyer distillation flask. Add 1-2 gm ferrous sulphate and 6 ml dilute sulphuric acid (1:1 v/v). Dilute to 75 ml and boil for 10-15 minutes.

B. Distillation Step

To the sample in the distillation flask (volume 50-75 ml) add 2 gm hydrazine hydrochloride (or hydrazine sulphate) and 2 gm of potassium bromide. Add a few glass beads, connect the flask to the distilling apparatus (Figure 1) and add 50 ml concentrated hydrochloric acid to the cup funnel. By means of a glass-marking pencil, mark the 100-ml, 150-ml, and 200-ml levels on a 300-ml tall form beaker. Put 100 ml of cold distilled water in the beaker and mount it on a block of wood so that the lower end of the condenser of the distillation apparatus dips well below the surface of the water. Turn on the cooling water to the condensers and set the hot plate switch to "High". Immediately run the acid into the distillation flask by opening the stopcock on the cup funnel. Leave the stopcock open and continue heating until 50 ml of distillate has been collected

*Alternatively sulphuric acid can be used to eliminate nitric acid. In this case dissolve the residue at this point in water. Add 2-3 gm of ferrous sulphate and 3 to 4 ml of sulphuric acid. Evaporate to sulphuric fumes. Cool, cautiously dilute with 20 ml of water and warm to dissolve. Filter (if necessary) into a 300-ml Erlenmeyer distilling flask, and boil to expel SO_2. Let cool and dilute to 50-75 ml.

in the beaker. Pour another 50 ml of concentrated hydrochloric acid, in small increments, through the cup funnel. Temporarily remove the wood block support and lower the beaker so that the top of the condenser is clear of the liquid surface (to prevent sucking back of the distillate as the result of cooling when the acid is added to the distillation flask). After a moment or two, replace the wood block to again support the beaker so that the condenser tip is immersed in the solution. Continue to heat until a second 50 ml of distillate has been collected. Remove the wood block and lower the beaker. Remove the distillation flask and rinse the inside of the condenser and the outside of the condenser tip into the beaker with a few ml of water.

C. Titration

1. *Bromate Method*

To the solution in the beaker add 10 ml concentrated hydrochloric acid, a small crystal of potassium bromide and 4 drops of Bordeaux indicator.

If the approximate amount of arsenic present is not known, begin the titration using the weak standard potassium bromate solution in a 10-ml burette. If there is no indication of the end-point being reached after adding 10 ml of the weak solution, change to a 50-ml burette containing regular standard potassium bromate solution. If the approximate amount of arsenic present is known, of course, use a burette of suitable size containing the standard solution suggested (Tables 1 and 2).

Titrate to the disappearance of the pink colour. When the colour begins to fade add 2 drops more of the indicator and continue to titrate to the end-point. Record the titration.

2. *Iodine Method*

Add a few drops of phenolphthalein indicator to the distillate and, stirring constantly, neutralize by cautiously adding 50% sodium hydroxide solution. Make the solution just acid by adding concentrated hydrochloric acid dropwise. Cool. Add 5 gm of solid sodium bicarbonate and stir well. Add 10 ml of starch solution, and titrate with standard iodine solution to the first permanent blue end-point. Record the titration in ml.

3. *Colorimetric Finish*

If the titration is less than 1 ml using the weak standard bromate solution, or if it is desired to complete the determination colorimetrically in any case, add 3 ml perchloric acid and 3 ml nitric acid to the distillate in the beaker and take to dryness. Continue with the procedure outlined in METHOD As–P_2O_5-2, calculate and report as described in that method.

Table 1

Table of Suitable Sample Weights, Solid Samples

Range, %	Sample Wt., gm	Titrate with
0.01 – 0.1	5	weak standard
0.1 – 1.0	5	regular standard
1.0 – 10	2	regular standard
10 – 50	0.5	regular standard

Table 2

Table of Suitable Sample Weights, Solution Samples

Range, gm/l	Sample Vol.	Titrate with
0.01–0.1	50	weak standard
0.1–1.0	50	regular standard
1.0–10	20	regular standard
10–50	5	regular standard

CALCULATIONS

$$\% \text{ As} = T \times f \times \frac{\text{dilution vol., ml}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

$$\text{gm/l As} = T \times f \times \frac{\text{dilution vol., ml}}{\text{aliquot taken}} \times \frac{1000}{\text{sample vol.}}$$

T = titration ml

f = factor, gm As per ml of titrant used.

If only a few drops of the weak titrant are required to titrate the final solution, the arsenic content is reported as less than the minimum amount detectable (an actual figure based on the sample weight and volume used) rather than using the term "not detected". The minimum amount detectable may be taken as 0.00025 gm As, and the figure to report may be calculated on this basis:

$$\% \text{ As} = \text{less than } 0.00025 \times \frac{\text{final solution volume}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

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The Colorimetric Determination of Arsenic and Phosphorus

METHOD As-P_2O_5-2

SCOPE

By the methods described, either phosphorus alone, or arsenic plus phosphorus (As + P_2O_5) may be determined in ores and mill products. Arsenic may be determined by difference if the ratio of P_2O_5 to As does not exceed about 5. When this ratio is exceeded, the distillation-bromatometric procedure (As-1) should be used. The latter method should also be used if the impurity content is high. For the lower ranges of arsenic concentration, it is possible to employ the decomposition and distillation steps of As-1, to eliminate interference, then complete the determination on the distillate using the colorimetric finish (in this case the one determination only), using the "As + P_2O_5" procedure.

RANGE

As little as 0.001 gm/l or 0.001% P_2O_5 may be determined. Arsenic can be determined in the same range, but the accuracy of this determination by the difference method will depend on the ratio of arsenic to phosphorus. High concentrations of phosphorus can be determined by the molybdate-titrimetric procedure (P-1), and for arsenic, the corresponding method is As-1.

OUTLINE

Arsenates and phosphates (as well as germanium and silicon) react with molybdate under suitable conditions to produce heteropoly compounds, for example ammonium molybdiphosphate $(NH_4)_3\ P\ (Mo_3O_{10})_4$. These can be reduced by means of a number of reducing agents, including stannous chloride (2), to molybdenum blue. This compound, whose exact composition may be variable and has been assigned a variety of formulae (5, 7) was first reported by Berzelius (1). The mechanism of its formation has been explained in various ways. The blue compound $(MoO_2)_2.MoO_4$ (5) or Mo_8O_{23} (7), contains no phosphorus or arsenic. Nevertheless only the molybdenum associated with these elements in the complex is reduced under the proper conditions of acidity. If this is too low, ammonium molybdate itself will be reduced, while if the acidity is too high, the blue colour will not be produced even if phosphate is present (4). For this reason it has been postulated that it is the ammonium salt, and not the free molybdiphosphoric or molybdiarsenic acid, which is reduced. The acid must be at least 0.35N to prevent reduction of the reagent. Interference from silica is also prevented by higher acidity. At an acid concentration of 0.40N, (used in the procedure given here), up to 700 ppm SiO_2 can be tolerated. Other writers (6) propose even higher acidities (1.7 to 2.4N) but in this case it becomes necessary to boil the solution to develop the colour.

Woods and Mellon (5) investigated interference very thoroughly. They found that aluminum, ammonium, beryllium, cerium (III), calcium, lithium, magnesium, manganese, potassium, sodium, and thorium (up to 500 ppm) do not interfere. Barium, lead, mercury (I or II), silver, strontium, and zirconium precipitate the molybdate. Antimony, bismuth, cadmium, chromium, copper, ferric iron, and zinc form soluble complexes and bleach the colour. However, an iron : arsenic or iron : arsenic + phosphorus ratio of 10 : 1 can be tolerated provided the sample is read within 5 minutes (11). Ferrous iron also interferes, probably behaving in the same way as ferric iron. If, however, the colour fades after 10 minutes, it can be restored by adding more stannous chloride.

Ceric ion interferes since it is an oxidant. Cobalt, nickel, and uranyl ions are stated to interfere by their own colour, but experience here definitely shows that exceedingly large amounts of uranium do not interfere.

Of the anions, acetate, benzoate, carbonate, formate, lactate, nitrate, perchlorate, salicylate, sulphate, sulphite, and tetraborate do not interfere up to 500 ppm. Such oxidizing and reducing anions as chlorate, chlorostannate, cyanide, dichromate, nitrite, thiocyanate, thiosulphate and vanadate interfere. The halogens, especially fluoride, and certain sequestering agents such as citrate, tartrate, and oxalate decrease the colour intensity. Tungstate and vanadate give a blue which is similar to molybdenum blue.

It was reported by Clausen and Schroyer (10) and by others (14), that the molybdenum blue colour does not give a straight Beer's law plot at any wave length between 400 and 800 mμ. This has been confirmed here. It has been found that a reasonably straight line is obtained over the range 0 to 0.25 absorbance units (corresponding to 0 to 50γ As or P_2O_5 in 100 ml, read in 1.5-cm cells). Assuming that the effect is due to agglomeration of colloidal molybdenum blue particles, an improved curve should be obtainable using 5-cm cells, and this seems to be so.

The method described does not include separations for the above interfering ions since, while the list is imposing enough, many of them are destroyed in the initial treatment. If it is considered necessary, the distillation procedure from As-1 can be utilized to separate arsenic substantially free of all interfering ions. For the determination of phosphate alone, arsenic is removed by volatilization from perchloric acid solution as the pentabromide, using hydrobromic acid. It is important that the last trace of hydrobromic acid be removed to prevent fading of the colour. This is accomplished by further fuming with perchloric acid, and no loss of phosphoric acid results, as is the case if sulphuric acid were to be used. Furthermore, ferric iron has relatively little colour in perchloric acid solution, so that interference from this source is reduced. In concentrations up to 2-3 ml per 100 ml of solution, perchloric has no effect on the intensity of the colour.

The removal of elements and ions other than arsenic, which would interfere in the phosphorus determination, does not form part of this method. It will be necessary to remove such interferences by a suitable method which will be found in the references (12, 13).

The method is very susceptible to salting, due particularly to the common use of phosphates as sequestering agents and builders in soaps and detergent mixtures. For this reason, all glassware should be cleaned using a pure detergent, such as the liquid non-ionics.

APPARATUS

Beakers, Griffin low-form:	250 ml size.
Watch glasses:	
Funnels, Bunsen long-stem, fluted:	65 mm dia.
Flasks, volumetric:	50, 100, 250, 500 ml sizes, (100 ml for colour development). Reserve a separate stock for this determination. Immediately after use, wash and rinse these flasks with distilled water and stopper them for storage. Avoid the use of phosphate for cleaning. Molybdenum blue stains can be removed with ammonia.
Pipettes, volumetric:	1, 2, 5 ml.
Flasks, Erlenmeyer:	125 ml size.
Water bath:	to maintain temperature at 25°C.
Colorimeter or Spectrophotometer:	
Colorimeter cells:	Clean frequently with ammonia to remove molybdenum blue deposits.
Gas burner:	Meker.

REAGENTS

Nitric acid:	
Perchloric acid:	in a dropping bottle.
Hydrobromic acid:	
Sodium sulphite solution:	10% w/v, in a dropping bottle.
Filter paper:	Whatman No. 30, 9-cm.
Ammonium hydroxide:	
Ammonium hydroxide, dil.:	1:1 v/v in a dropping bottle.
Methyl orange indicator:	0.05% w/v aq. solution.
Molybdate reagent:	(a) Into 800 ml water at 55 to 65°C, put 100.0 gm ammonium molybdate (crystals, reagent grade), and stir to dissolve without further heating. Allow to cool. (b) In a 4000 ml beaker, add 1120 ml sulphuric acid to 1800 ml water, taking the usual precautions. Allow to cool. When both solutions are cooled to room temperature, add solution (a) to solution (b), mix, and make up to 4000 ml (using a 2000 ml graduate). Mix thoroughly by pouring from one beaker to another several times. Store in bottles with glass stoppers or plastic caps. For rapid dispensing, store in a 4 litre aspirator bottle connected by Tygon tubing to a 50 or 100 ml automatic burette. This avoids contamination of the reagent.
Stannous chloride solution:	This solution is prepared fresh weekly. To 2.50 gm stannous chloride ($SnCl_2.2H_2O$) in a 100 ml beaker, add 10 ml HCl. Dissolve the salt, warming slightly if necessary. Cool. Dilute with water to 100 ml in a graduate. Keep in a cool place in a tightly-stoppered dark-glass dropping bottle.
Detergent:	phosphate-free for cleaning glassware.
Standard phosphate rock:	NBS 56b 31.55% P_2O_5.
Standard arsenic solution:	Take 0.132 gm As_2O_3 just to fumes with 5 ml of perchloric and 2 ml of nitric acid. Cool and dilute to 100 ml. 1 ml = 1.00 mg As. Dilute as required to prepare the standards.

Preparation of the Calibration Graph

For the arsenic curve, prepare appropriate solutions from the standard arsenic solution and take aliquots containing from 5 to 50 gammas arsenic.

For the phosphorus curve, treat standard samples of phosphate rock as for solid samples, and take aliquots containing from 5 to 50 gammas P_2O_5.

Develop the colour as described in the procedure and plot a graph of absorbance or transmittance as ordinate against γ As or P_2O_5 per 100 ml volume as abscissa in 1-cm and in 5-cm cells. Note that the colour does not obey Beer's law over the whole range.

PROCEDURE

A. Arsenic plus Phosphorus (As + P_2O_5)

1. *Preparation*

(a) *Solid Samples*—Place 0.5- to 2-gm sample in a 250-ml beaker. Add 5 ml nitric acid, 5 to 10 ml perchloric acid (add the nitric first), and swirl to disintegrate lumps. Boil for 15 minutes and evaporate to copious fumes of perchloric acid. Allow to fume for 30 to 60 seconds, but no longer. Cool. Rinse the cover glass and the sides of the beaker with a little water, add about 30 ml more water, and boil for a few minutes. Filter through a No. 30 paper into a volumetric flask (for size of flask, *see* "Table of Dilution"). Wash with hot water. Cool, dilute to the mark with water, and mix. Dilute further if indicated in the table.

(b) *Residues, for Entrained Organic Phosphate* (15)—Take 2-5 grams of sample, (since 1 lb. of solvent mixture per ton of ore is equivalent to only 0.001% P_2O_5). Treat the samples in the same way as described under solid samples, but attack the sample first with 20 ml of a mixture of 3 parts of nitric acid and 1 part of perchloric acid. Take to copious fumes of perchloric acid and proceed with the balance of the procedure as outlined, but use the whole sample for colour development. It is not necessary to include the arsenic removal step unless arsenic is known to be present in the ore.

(c) *Solution Samples*—Pipette the sample into the volumetric flask, add 1 or 2 ml perchloric acid, dilute and mix. If halogens, tartrate, etc., may be present, fume the sample with nitric and perchloric acids in a small Erlenmeyer flask. This should also be done if the phosphorus is not known to be present as orthophosphate.

If much organic matter is present, fume briefly with nitric and sulphuric acids, then cool, add perchloric acid, and fume again.

2. *Development of Colour*

Pipette an aliquot containing 15 to 45 gammas (micrograms) of As + P_2O_5 into one of the 100-ml volumetric flasks reserved for this purpose. Make up to about 80 ml with water. Add 3 drops methyl orange. Neutralize with ammonium hydroxide (to a 1-drop end-point with 1:1 ammonium hydroxide). Add 4.0 ml molybdate solution. *Mix well.* Adjust the temperature to between 24 and 26°C. Dilute with water until the *top* of the meniscus is at the mark (leaving room for the addition of the stannous chloride).

Noting the time, add 6 drops stannous chloride solution and mix well. Read the transmittance when it reaches a minimum; this takes from 6 to 15 minutes. With the Cenco-Sheard Photoelometer use the "D" filter (87309D); with the Bausch and Lomb instrument, use the 630 mμ filter.

From the standard curve for arsenic, prepared as directed above, read the amount of "As + P_2O_5", as arsenic.

B. Phosphorus (P_2O_5)

Into a 125-ml Erlenmeyer flask, pipette the sample of solution to be tested, or the first aliquot from the ore solution. Add 5 ml hydrobromic acid and 5 ml perchloric acid. Heat moderately on the hot plate until fumes begin to appear. Then heat, with constant motion, over an open flame until copious fumes are evolved, the interior of the flask becoming free from visible fumes. Cool. Take up in a little water. Dissolve any MnO_2 with a drop of Na_2SO_3 solution. Transfer to the flask required for the next dilution (filtering if necessary). Proceed as for As + P_2O_5, under "Development of Colour". Read the phosphorus content, as P_2O_5, from the standard curve for phosphorus obtained as directed above.

C. Arsenic Alone (As)

Read the phosphorus transmittance on the arsenic curve, and calculate the % or gm/l "as arsenic". Subtract this figure from the % or gm/l "As + P_2O_5", as described under "Calculations".

Table of Dilutions

Solution Samples		*Solid Samples*	
gm/litre	*Dilution and Aliquot*	*Per cent*	*Dilution and Aliquot*
under 0.02	2 ml (direct)	under 0.02	2 gm/100 x 10
.02 – .04	1 ml (direct)	.02 – .04	2 gm/100 x 5
.03 – .09	5/ 50 x 5 ml	.04 – .10	2 gm/100 x 2
.06 – .20	5/100 x 5 ml	.10 – .25	2 gm/250 x 2
.15 – .45	5/100 x 2 ml	.2 – .5	1 gm/250 x 2
.4 – 1.2	2/100 x 2 ml	.8 – 2.0	1 gm/500 x 1
1.0 – 3.0	2/250 x 2 ml	1.5 – 4.0	0.5 gm/500 x 1
2.0 – 6.0	2/250 x 1 ml	2.5 – 7.5	2 gm/250 x 2/100 x 5
4 – 12	1/250 x 1 ml	5 – 15	2 gm/250 x 2/100 x 2
		12.5 – 35	2 gm/250 x 2/100 x 1

CALCULATIONS

As + P_2O_5 Calculation

From the standard curve for arsenic, which has been plotted as micrograms (gammas) of As per 100 ml vs. transmittance, read the As + P_2O_5 content as arsenic. Then As + P_2O_5 content, as arsenic, is given by:

For Solid Samples

$$\% \text{ As} + P_2O_5 \text{ (as arsenic)} = \frac{\gamma \text{ As/100 ml (graph)}}{1{,}000{,}000} \times \frac{\text{final sol'n volume}}{\text{aliq. taken}} \times \frac{100}{\text{sample wt.}}$$

For Solution Samples

gm/l As + P_2O_5 (as arsenic) =

$$\frac{\gamma \text{ As } 100 \text{ ml (graph)}}{1{,}000{,}000} \times \frac{\text{final sol'n vol.}}{\text{aliq. taken}} \times \frac{1000}{\text{sample vol.}}$$

If the sample gives approximately the same reading as the reference solution, the amount of As + P_2O_5 shall be reported as less than the minimum amount detectable (an actual figure based on the sample weight and volumes used). The minimum amount detectable may be considered as 15 micrograms As per 100 ml, and the figure to report may be calculated on this basis; for example

$$\%\ \text{As} + P_2O_5 = < \frac{15}{1{,}000{,}000} \times \frac{\text{final sol'n vol.}}{\text{aliq. taken}} \times \frac{100}{\text{sample wt.}}$$

P_2O_5 Calculation

From the transmittance, read the P_2O_5 content in micrograms per 100 ml from the P_2O_5 graph in the same manner as described above for As. If no colour is obtained, report the content as less than the minimum amount detectable, also calculated as described above.

As Calculation

Having obtained the transmittance for As + P_2O_5 and for P_2O_5 above, read them both on the arsenic graph. Calculate the gm/l or % of each in the original sample as previously described. The difference between the two figures is the arsenic content. The ratio $\frac{\text{As}}{\text{As} + P_2O_5}$ must be at least 0.2 to be significant (since the error in each of the two figures whose difference is to be taken is of the order of 5%). This ratio must be checked, and if it is found to be less than 0.2, the result shall be reported as "less than" the value actually calculated, or shall be qualified by the word "approximately". If the phosphorus content is high, arsenic should be separated by distillation prior to colorimetric determination.

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Methods for Evaluating Used Anion Exchange Resins

METHOD A.X.–1

SCOPE

The following group of methods is intended for use in assessing the extent to which ion exchange resins have deteriorated in use. Strictly quantitative evaluation is not possible, but the results of the tests can be used to suggest possible means for treating badly deteriorated resins to restore them to usefulness.

OUTLINE

Anion Exchange Capacity Measurements

This method determines both weak and strong base capacities on a single sample of resin. The resin is first converted completely to the chloride form. The weak base groups are then regenerated by passing ammonium hydroxide which converts them to the hydroxyl form, and liberates a corresponding amount of the chloride which is determined in the eluate. Ammonium hydroxide has no effect on the strong base groups. The salt-splitting or strong-base capacity is then determined by passing sodium sulphate solution. The sulphate ion displaces the chloride practically stoichiometrically. Titration of this chloride therefore will give the strong-base capacity. The total anion exchange capacity is the sum of these two capacities. If only a total anion exchange capacity is wanted, the ammonia treatment can be omitted and the rinsed chloride form leached directly with sodium sulphate solution (1).

It is not certain that there actually are weak-base groups on these resins; it has been suggested that they are merely strong-base groups that are hindered in one way or another. The importance attached to their presence results from the fact that (as can be seen from the above discussion) they can exchange sulphate for chloride, but are incapable of taking up uranium. They therefore use up chloride from the eluting solution to no purpose.

Polythionates

A caustic solution will strip polythionates from an anion exchange resin, at the same time decomposing them and liberating a corresponding amount of thiosulphate which can be titrated with iodine. The reactions are described in METHOD S_nO_6–1.

The other methods given are more or less routine in nature. They have for the most part been abstracted from reports issued by the Rohm and Haas Co., Pittsburgh, Pa., the manufacturers of the resin IRA 400 (2).

A general discussion of the symptoms and treatments for poisoning will be found in the paper by Nugent (3).

APPARATUS

Ion exchange columns:	It is *important* that the resin bed should not be too short. A bed depth of 12″ or more is recommended and the following internal diameters for the columns are suggested. ¼″ for 10 cc ⅜″ for 25 cc ½″ for 50 cc ¾″ for 100 cc Fischer and Porter Ultra-max chromatographic columns are suitable —Burettes of suitable size with glass stopcocks can be used, if a plug of glass wool is inserted to support the resin bed.
Glass wool, Pyrex fine:	
Quartz sand, 20 mesh:	
Crucibles, filtering, sintered glass:	60 ml size, coarse frit.
Dishes, evaporating, Vycor:	100 ml size.
Crucibles, platinum:	60 ml size.
Flasks, Erlenmeyer:	250 ml size. 1000 ml size.
Filter paper:	Whatman No. 41 H, 15-cm size.
Funnels, filtering, Bunsen, long stem:	100 mm dia.
Flasks, volumetric:	1000 ml size.
Funnels, separatory, Squibb pear-shaped:	1000 ml size.
Funnel support:	for filtering funnels.
Funnel support:	for separatory funnels.
Pipettes, volumetric:	50 ml size.
Stopwatch:	for timing flow rates.

REAGENTS

Standard eluting solution (for preliminary treatment of resin only):	For each litre required, dissolve 39 gm NaCl in 500 ml water, add 28 ml of concentrated hydrochloric acid, and make to the required volume with water.
Hydrofluoric acid, 48% C.P.:	
Sulphuric acid, concentrated:	
Sulphuric acid, dil., 1:1 v/v:	
Sulphuric acid, 5% v/v:	Cautiously add 100 ml dil (1:1) H_2SO_4 to 500 ml of water with constant stirring and make to 1 litre.
Sulphuric acid, 10% v/v:	Cautiously add 200 ml dil (1:1) H_2SO_4 to 500 ml water with constant stirring and make to 1 litre.
Sodium hydroxide, 5% w/v:	
Sodium hydroxide, 10% w/v:	
Formaldehyde, 40% reagent:	
Iodine solution, 0.004N:	Add 40 ml of standard N/10 iodine to a 1000 ml volumetric flask by means of a burette, make to volume and mix well.
Chloroform C.P.:	

Hydrochloric acid, 4% w/v:	Dilute 120 ml concentrated hydrochloric acid to 1 litre.
Ethanol, 95%:	*Not* denatured.
Ammonium hydroxide, concentrated:	
Ammonium hydroxide, 1% v/v:	Dilute 10 ml concentrated ammonium hydroxide to 1 litre.
Sodium sulphate solution, 4% w/v:	Dissolve 40 grams anhydrous sodium sulphate in water and dilute to 1 litre.
Standard uranium loading solution, 1 gm/l U:	Dissolve 1.76 gm $UO_2SO_4.3H_2O$ and 44 gm Na_2SO_4 (anhydrous) separately in water for each litre of solution required. Dilute to the required volume. Adjust the pH to 1.8 with dil (1:1, v/v) sulphuric acid (takes about 3.5 ml per litre). Have the solution assayed for U and for SO_4, adjust to exactly 1 gm/l U and 30 gm/l SO_4 and readjust pH if necessary.
Hydrochloric acid eluting solution, 1M:	Take 86 ml concentrated hydrochloric acid for each litre required and dilute to volume.
Nitric acid eluting solution, 1M:	Take 65 ml of concentrated nitric acid for each litre required and dilute to volume.
Salt: sulphuric eluting solution:	Take 58 gm NaCl for each litre required. Dissolve in water and add 5.6 ml of dil (1:1 v/v) sulphuric acid for each litre required. Dilute to volume.

PROCEDURE

A. Preliminary Treatment

Prior to any analyses, convert an amount of resin sufficient for all analyses to the chloride form by passing through it, a solution which is 2/3 N in NaCl and 1/3 N in HCl.

If the resin has previously been used for uranium adsorption, pass sufficient of this solution through to get a negative test for uranium i.e. at least 10 bed volumes. If fresh resin is used pass about 5 bed volumes of solution through. Use a flow rate of about 10 ml/min for 100 ml of resin in a $\frac{3}{4}$-inch diameter column.

Following conversion to the chloride form, rinse the resin with distilled or deionized water until it is free from sodium.

B. Moisture

Pour 20 ml of the conditioned resin into a sintered glass filtering crucible and remove the excess water using suction (for 5 minutes). Weigh the crucible and resin to obtain weight of "suction dried" resin. Dry at 110°C for 24 hours and report the loss in weight as % moisture.

C. Sulphated Ash

Divide the dried resin from the moisture determination into two approximately equal portions and transfer to previously ignited and weighed 100-ml Vycor evaporating dishes. Weigh to obtain the exact weight of resin.

Moisten the resin with concentrated sulphuric acid and fume to dryness. Repeat if necessary. Ignite the residue until free of carbon, cool, moisten the

residue with concentrated sulphuric acid and fume to dryness. Finally ignite at dull red heat to remove the last traces of sulphuric acid. Cool, weigh and report % sulphated ash on the dry basis.

Submit the ash of one sample for spectrographic analysis and reserve the other for the silica determination.

D. Silica

Take up the ash from the sulphated ash determination in about 50 ml of 5% sulphuric acid. Filter on ashless paper and wash with dilute sulphuric acid. Ignite in a platinum crucible. Cool and weigh. Treat the residue with 1 ml of 1:1 sulphuric acid and 5 ml of hydrofluoric acid. Take to dryness. Repeat this treatment twice and finally ignite. Cool and reweigh. The loss in weight is reported as "% silica" on the dry basis.

E. Polythionates

Transfer approximately 10 ml of the conditioned resin to a burette with a glass wool plug. Backwash and drain to settle resin. Elute the resin with 10% w/v sodium hydroxide solution collecting approximately 100-ml fractions of the eluate in Erlenmeyer flasks at a 1 ml/minute rate. Add 5 ml of 40% formaldehyde, acidify with 10% v/v sulphuric acid, and add 10 ml in excess. Add a few ml of chloroform and titrate with 0.004N iodine and solution until the chloroform becomes pink. Continue these titrations until 100 ml of effluent requires less than 1 ml of iodine solution.

Wash the resin with distilled water until free from NaOH, and convert to the chloride form with 40 ml of 4% w/v HCl. Wash with 20 ml water, transfer to a sintered glass filtering crucible and dry at 110°C for 24 hours.

$$\% \text{ S (as } S_4O_6) = \frac{\text{total meq. of iodine required} \times 0.0853 \times 100}{\text{grams of dried resin}}$$

The above calculation is based on the assumption that the polythionate was present on the resin as $S_4O_6^=$ and the following reaction takes place when the resin is eluted with alkali.

$$2\ S_4O_6^= + 6\ OH' \longrightarrow 3\ S_2O_3^= + 2\ SO_3^= + 3\ H_2O$$

F. Chloride Capacity

Combined Procedure for Weak Base Anion Exchange Capacity and Salt-Splitting Anion Exchange Capacity

Transfer about 10 ml of the conditioned resin to a funnel fitted with a Whatman No. 41 H filter paper. Place 1 litre of 4% w/v HCl in a 1-litre separatory funnel and support it above the resin. Allow the acid to drip onto the resin, making sure the resin is covered with solution all the time. Discard this acid. Rinse the resin and paper with water a few times to remove most of the free chloride.

Rinse the separatory funnel with water to remove chloride and fill with 1 litre of 95% ethanol. Wash the resin with the ethanol in the same manner as before and discard the filtrate. Place a clean 1-litre volumetric flask under the resin funnel. Rinse the separatory funnel and fill with 1 litre of freshly prepared 1% v/v ammonium hydroxide solution. Pass just less than 1 litre of the hydroxide solution over the resin. Dilute exactly to volume and determine the chloride in an aliquot by the procedure given below.

Place a clean 1-litre volumetric flask under the resin funnel and fill the separatory funnel with 1 litre of 4% w/v sodium sulphate solution. Pass just less than 1 litre of the sulphate solution over the resin. Dilute exactly to volume and determine the chloride in an aliquot by the procedure given below.

Method for Determination of Chloride

REAGENTS

Standard mercuric nitrate solution:	Dissolve 17 grams $Hg(NO_3)_2$ in 50 ml of water containing 3 ml of concentrated HNO_3 and dilute to 1 litre.
Phosphate buffer solution:	Dissolve 13.6 grams of KH_2PO_4 in 1 litre of water and adjust pH to 2.0 with nitric acid.
Ferric sulphate or ferric nitrate solution:	5% in 1% HNO_3.
s-diphenylcarbazide or diphenylcarbazone indicator:	Saturated alcoholic solution—prepared fresh.
Standard sodium chloride solution:	0.100N.
Phenolphthalein indicator:	

Procedure

Take an aliquot sufficient to give a 5-10 ml titration and dilute, if necessary, to 100 ml with water. Add 1 drop of phenolphthalein indicator and add nitric acid until the pink colour is discharged. Add 1 drop of ferric sulphate (or nitrate) solution, 1 drop of diphenylcarbazide solution and 5 ml of buffer solution. Titrate with standard mercuric nitrate solution. Standardize the mercuric nitrate solution with the standard sodium chloride using a 10- to 25-ml aliquot of the chloride solution. Run a blank.

G. Restorability of Resin

Transfer 15 ml of the conditioned used resin to a 50-ml burette fitted with a flat glass wool wad. Pass 10 bed volumes (150 ml) of 10% w/v of sodium hydroxide solution at the rate of 0.5 ml/min.

Rinse with water until free of sodium hydroxide and pass 2 bed volumes (30 ml) of 4% w/v hydrochloric acid.

Redetermine the weak base and salt-splitting anion exchange capacities.

H. Uranium Capacity

Place 50.0 ± 0.5 ml of the conditioned resin in a ½-inch diameter glass column which has a coarse sintered glass disk sealed in near the bottom to support the resin. Backwash to fluidize the bed and drain without tapping or agitating at about 10 ml/min. Adjust resin volume, if necessary, and repeat. At the same time prepare a similar bed of fresh resin from the same lot and carry through the same loadings and elutions as the used resin.

Prepare sufficient head solution for the number of samples and tests required (about 8 litres per test). (*See* "Reagents").

The head solution used consists of 1.0 gram of U/l as pure uranyl sulphate and 30.0 grams of SO_4/l as sodium sulphate, adjusted to a pH of 1.8 with sulphuric acid.

Starting first thing in the morning, pass head solution through the column at 6.7 ml/min. Take regular samples and assay for uranium. Note the volume of solution passed to breakthrough (including any samples taken).

Continue passing solution until the effluent concentration is equal to 90% of the influent concentration.

Check for breakthrough and saturation while the column is running, using the visual fluorimeter, the thiocyanate or peroxide colorimetric methods, taking a concentration of 0.05 gm U/l in the effluent as breakthrough.

Rinse the loaded bed with 1 bed volume (50 ml) of water at 6.7 ml/min. Elute with M HCl, M HNO_3, or M salt-sulphuric acid (depending on system used in pilot plant work) at 2 ml/min and collect 1 litre (i.e. 20 bed volumes) in a volumetric flask. Assay this for U_3O_8 by a differential spectrophotometric procedure. Report the "as received" breakthrough and saturation capacities as grams U_3O_8 per litre of wet settled resin. Note the "nil spot" in elution (approximately 0.1 gm U_3O_8/l) using potassium ferrocyanide spot paper. Report the values for the fresh resin in the same manner.

Determine the "restored" uranium capacities as follows:

Rinse the resin after the above elution with 2 bed volumes of water (100 ml) at 2 ml/min. Restore with 3 bed volumes (150 ml) of 5% w/v NaOH solution at 0.32 ml/min. Rinse again with 2 bed volumes of water. Sulphate the resin with 2 bed volumes of 5% v/v sulphuric acid solution at 2 ml/min. and rinse with water to an effluent pH 2.

Re-load and elute the resin as before. Report the "restored" breakthrough and saturation capacities as grams U_3O_8 per litre of wet settled resin.

Report the results also for the fresh resin from the same lot.

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The Colorimetric Determination of Boron

METHOD B-1

SCOPE

This method is intended for the determination of very small amounts of boron in products and in the raw materials used to prepare them, for specification purposes.

RANGE

The method covers the range 0.0010% (10 ppm) and up. Smaller amounts could be determined by suitable modifications.

OUTLINE

Boron is determined colorimetrically by the colour it forms with 1, 1-dianthrimide in concentrated sulphuric acid solution at a wave length of 620 mμ (1, 2). The method omits the customary distillation procedure for isolating boron as methyl borate (3). Instead, interfering cations are removed by absorption on a strongly acid (nuclear sulphonic or methylene sulphonic) cation exchange resin (4). Certain cations, such as sodium, potassium, calcium, magnesium, zinc, copper, manganese, aluminum, and beryllium, do not interfere in any case, and if these only are present, the ion exchange step can be omitted.

Of the anions, sulphate, chloride, tungstate, arsenate, and arsenite do not interfere. Nitrate and nitrite would alter the colour of the reagent, but are removed in the fuming just before colour development. Oxidizing anions, such as vanadate, chromate, periodate and perchlorate interfere. Of these, only vanadate occurs commonly. It may be reduced to vanadyl prior to cation exchange, so that it is absorbed by the resin (4). Alternatively, the anions may be removed by ion exchange, using a mixed bed which combines a weak-base anion exchange resin with the cation exchange resin (5, 6).

The actual range is 4γ to 10γ. The sample is diluted to 250 ml after the ion exchange step and the sample size should be chosen so that a 5- or 10-ml aliquot may be taken for the final determination. Larger aliquots may lose boron by volatilization as boric acid during concentration prior to colour development.

The reagent (1, 1-dianthrimide) is very sensitive to traces of water in the sulphuric acid, and care must be taken to ensure that all apparatus in which it is handled is *dry*.

Temperature control during colour development is most important. The oven used should be adjusted by means of a thermometer on the shelf which is used to hold the samples and periodic checks of the temperature should be made during the 3-hour colour development period.

APPARATUS

Beakers:	Vycor 250 ml (Corning No. 728 Alkali-Resistant glass will not stand the heat required and platinum has not given good results.)
Crucibles:	30 ml platinum.
Flasks, volumetric:	Exax 250 ml. Exax 100 ml. Exax 25 ml. *oven-dried*
Columns for ion exchange:	1″ diam. Jones Reductor columns containing 150 ml wet settled resin supported on a glass wool pad.
Spectrophotometer:	Beckman Model B or DU.
Spectrophotometer cells:	1 cm light path Corex cells.

REAGENTS

Hydrochloric acid concentrated:	Reagent grade.
Saturated lime suspension:	Saturated aqueous solution containing a slight excess of C.P. calcium hydroxide.
Tri-acid mixture:	750 ml water, 250 ml sulphuric acid, C.P., 300 ml hydrochloric acid C.P. and 300 ml nitric acid.
Sodium carbonate, anhydrous:	Reagent grade.
Sulphuric acid, 10%:	100 ml solution, containing 10 ml concentrated sulphuric acid.
Sulphuric acid concentrated:	
Cation exchange resin, IR 100 or IR 120 hydrogen forms:	Regenerate the resin when required, with 10% w/v hydrochloric acid until the eluate tests negatively for cations. (For iron and uranium, spot-test with 20% potassium ferrocyanide reagent.) Wash free of acid with water.
Anion exchange resin, IR 4B hydroxyl form:	Regenerate the resin when required with 5% w/v sodium hydroxide, spot-testing for vanadate or any other ion absorbed. Wash free of hydroxide with water.
Standard boron solution, 1 ml = 1μ gm B:	0.5715 gm orthoboric acid in 1 litre of water. Dilute 1 ml to 100 ml for use—1 ml = 1 μ gm B.
1, 1-dianthrimide:	Dissolve 20 mg in 200 ml concentrated sulphuric acid. Make up fresh as needed.

Preparation of Calibration Graph

Take aliquots of the diluted standard boron solution, corresponding to 2, 4, 6, 8 and 10 μ gm. Transfer to 250-ml Vycor beakers, and add 5 ml concentrated sulphuric acid. Carry out a blank determination. Heat just to fumes and cool. Add 12.5 ml of freshly prepared 1, 1-dianthrimide solution and heat at 90°C for 3 hours, maintaining this temperature very carefully in a thermostatically-controlled oven by means of a thermometer on the same shelf as the beakers. Cool in a desiccator and transfer to oven-dried 25-ml volumetric flasks. Dilute to the mark with concentrated sulphuric acid. Read the samples at 620 mμ on the Beckman B spectrophotometer using 1-cm cells, against water in the reference cell. Subtract the blank reading and plot a curve of absorbancy as ordinate vs. concentration (μ gm boron in 25 ml) as abscissa. (Note: The Beckman DU spectrophotometer may also be used and since it is more sensitive, the samples may be read against the reagent blank in the reference cell, eliminating the necessity for a separate blank correction.)

If it is desired to eliminate the ion exchange step, with samples which do not contain seriously interfering elements, draw up a calibration curve using a boron-free matrix approximating the composition of the material to be tested and containing known amounts of boron. Boron frequently can be removed by treating the dry material with a dry methanolic solution of hydrochloric acid gas. Two or three evaporations may be necessary. A blank of the boron-free material should also be carried through the procedure for calibration and through the analytical procedure.

PROCEDURE

A. Decomposition and Sample Preparation

1. *Readily Soluble Materials*

Weigh a sample containing between 100 and 200 μ gm boron (usually about 5 gm) and transfer to a Vycor beaker. Add about 10 ml distilled water, wetting the sample completely. Add 5 ml cold concentrated hydrochloric acid, and let stand 10 minutes with occasional swirling. If solution is not complete (except for small amounts of silica etc.) add a further 1 ml of hydrochloric acid (but no more), swirl, and let stand 10 minutes with occasional swirling. If solution is not complete (except for small amounts of silica etc.) add a further 1 ml of hydrochloric acid (but no more), swirl, and let stand for 5 minutes longer.

Make the solution to 50 ml with water and filter through a fast paper (Munktell 1 F or Whatman 41 H) into a 250-ml Vycor beaker. If a substantial residue remains, treat it by "Refractory Material or Siliceous Residue" method (which follows), adjusting the amount of sodium carbonate used according to the size of the residue.

Determine the boron in the soluble and insoluble portions separately, or combine the cooled carbonate melt with the soluble portion and add the calculated amount of hydrochloric acid required to react with the sodium carbonate.

2. *Non-Refractory Materials Not Readily Soluble in Hydrochloric Acid* (1)

Weigh a 1-gram sample into a 250-ml Vycor beaker, and add 6 ml saturated lime suspension. Dissolve the sample in 5 ml of the tri-acid mixture. Cool and make to 100 ml in a 250-ml Vycor beaker.

3. *Non-Refractory Materials Containing Organic Matter*

Weigh a 2-gm sample into a 250-ml Vycor beaker. Moisten with water and add 5 ml of dilute sulphuric acid (1:1), v/v. Mix well and add 10 ml of a lime suspension containing about 10 gm Ca $(OH)_2$ per litre. Evaporate just to fumes of sulphur trioxide—this will cause the organic matter to char. Let cool slightly and add 5-10 drops of concentrated nitric acid to the still hot solution. Repeat the fuming and nitric acid treatment until the organic matter is destroyed. Fume again to remove the bulk of the nitric acid. Cool, dilute to 100 ml and proceed to Section B "Separations".

4. *Refractory Material or Siliceous Residue*

Weigh a 1-gram sample (or in the case of the siliceous residue from a sample dissolved by the preceding method, the whole of the dried residue) into a 25-ml platinum crucible. Add six times the weight of residue, (accurately weighed) of anhydrous sodium carbonate, A.R. Mix well and fuse over a gas burner for the minimum time required to give complete solution. Cool, transfer the melt completely to a Vycor beaker, washing the crucible thoroughly with water. Dissolve in the calculated amount of concentrated HCl (about 8 to 10 ml) at

room temperature. Filter if necessary through a fast paper into a 250-ml Vycor beaker, and make to 100 ml.

B. Separations

1. *Removal of Interfering Cations by Ion Exchange*

If interfering cations are known to be absent (e.g. analysis of MgO or NaCl) omit this step and make the solution up to 100 ml in a volumetric flask with no other treatment.

Otherwise, dilute the solution from the previous step, or in the case of a solution sample, a suitable aliquot of the sample, to 100 ml with water. Pass through a Jones Reductor column containing 150 ml wet settled IR-100 or 120 (hydrogen form) supported on a pad of glass wool. (Note: This column can be used for two 5-gm samples of the uranium product without regenerating.) Use a flow of about 3 drops per second (8-9 ml per minute). Never let the solution level drop below the top of the column or channelling will occur. Wash the sample through the column with 100 ml water at the same flow rate, collecting the washing in the same beaker. Transfer to a 250-ml volumetric flask, make to volume, and mix well.

2. *Simultaneous Removal of Interfering Cations and Anions by Mixed Bed Ion Exchange.*

If interference is suspected due to the presence of oxidizing anions such as CrO_4^{-2}, MnO_4^-, VO_3^- and NO_3^-, use the following ion exchange step:

Regenerate a column of IR-120 resin in the hydrogen form with 10% w/v hydrochloric acid and in another column regenerate a bed of IR-4B (weak-base) resin in the hydroxyl form using 1000 ml of 5% NaOH solution. Wash each resin with water and dry in the oven (100°C). Grind equal quantities of each resin in a mortar to a medium fineness and slurry into a column.

After washing the bed with several hundred cc. of distilled water, run the dissolved samples through the column as above, ("Removal of Interfering Cations by Ion Exchange"). The column should be able to absorb about half the amount of cations absorbed by the equivalent strong acid bed and must be discarded on saturation. Draw up a separate graph using standards made from a solution of 200γ B passed through the mixed bed exchanger to check recovery.

C. Colour Development

Transfer a 10-ml aliquot of the sample solution to a 250-ml Vycor beaker and add 5 ml concentrated sulphuric acid. Take just to fumes, slowly, using low heat. Cool, add 12.5 ml of 1, 1-dianthrimide working solution and heat in a drying oven at 90°C for 3 hours. (This has been found to give maximum colour development.) This temperature must be very carefully controlled. Prepare a reagent blank using 12.5 ml of 1, 1-dianthrimide working solution and 5 ml concentrated sulphuric acid, heat in the drying oven and carry through the balance of the procedure with the samples. Cool in a desiccator, transfer to an oven-dried 25-ml volumetric flask and make to volume with concentrated sulphuric acid. Read absorbance at 620 mμ on a Beckman "B" spectrophotometer using 1-cm cells against water in the reference cell. Subtract the blank reading from the sample reading and determine γ B per 25 ml from a previously prepared calibration curve.

CALCULATIONS

Solid Samples

$$\% \text{ B} = \frac{\gamma\text{B per 25 ml (from graph)}}{1{,}000{,}000} \times \frac{\text{final sol. volume}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

Solution Samples

$$\text{gm/l B} = \frac{\gamma\text{B per 25 ml (from graph)}}{1{,}000{,}000} \times \frac{\text{final sol. volume}}{\text{aliquot taken}} \times \frac{1000}{\text{sample vol. taken}}$$

If the sample gives approximately the same reading as the blank, the amount of boron should be reported as less than the minimum amount detectable (an actual figure based on the sample weight and volume used) rather than using the term "not detected". The minimum amount detectable may be considered as 1 microgram B per 25 ml volume for colorimetric reading using 1-cm cells and the figures to report may be calculated on this basis, e.g.

$$\% \text{ B} = \text{less than } \frac{1}{1{,}000{,}000} \times \frac{\text{final solution volume}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

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The Gravimetric Determination of Bismuth as Bismuth Oxychloride

METHOD Bi-1

SCOPE

The methods given below are applicable to all types of ores, mill products and solutions containing bismuth in amounts high enough to be determined gravimetrically.

RANGE

From 2 mg to 200 mg of bismuth can be determined.

OUTLINE

Bismuth oxychloride is precipitated by neutralizing a nitric acid solution of the element with ammonium hydroxide, adding a few drops of hydrochloric acid, diluting with water and digesting on a steam bath. Large amounts of lead removed as the sulphate, or silver removed as the chloride, will carry down small amounts of bismuth. If these separations are used, double precipitations should be made. Elements that hydrolyze readily or precipitate as chlorides in weak acid solutions interfere. These include antimony, tin, zirconium, thallium, univalent mercury, silver, niobium, etc.

Copper, cadmium and small amounts of lead do not interfere.

$$BiCl_3 + H_2O \longrightarrow Bi\,OCl + 2\,HCl$$

Compounds that form insoluble compounds with bismuth must be absent. These include sulphates, arsenates, phosphates and iodides.

Lead (which is often present in bismuth-containing material) can be removed by precipitation as sulphate. At the same time silica can be dehydrated and removed. If large amounts of lead are present, the step should be omitted since it can lead to loss of bismuth in the insoluble residue.

Treatment with hydrogen sulphide precipitates bismuth, silver, lead, copper, arsenic, antimony and tin (lead is not completely precipitated). Washing with ammonium sulphide (in which bismuth sulphide is insoluble), removes arsenic, antimony and tin. Treatment with potassium cyanide then removes copper and silver (it would also remove arsenic, antimony and tin).

By dissolving the precipitate in dilute nitric acid, mercury (being insoluble) is left behind.

When the amount of bismuth exceeds 5 mg it is better to precipitate the bismuth as the basic carbonate, and ignite it to the oxide. The oxychloride precipitate is dissolved in hot dilute nitric acid and most of the chloride removed

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by evaporation to a syrupy consistency. The solution is diluted and the excess acid nearly neutralized with ammonium hydroxide. A slight excess of ammonium carbonate is then added and the solution digested until the basic carbonate precipitates. Lead, thallium, mercury, sulphates, chlorides and phosphates interfere. They will have been eliminated, however, by the preliminary treatment described above in connection with the oxychloride method. Cadmium and copper do not interfere and are in fact separated from bismuth by the basic carbonate separation.

Bismuth oxides and salts dissolve readily in hydrochloric, nitric and sulphuric acids. The hydrochloric-hydrobromic acid mixture gives rapid decomposition of sulphidic ores.

APPARATUS

Beakers, Griffin low-form:	250 ml size.
Beaker covers, watch glass and Speedyvap:	
Funnels, Bunsen filter, long-stem, fluted:	65 mm. dia.
Funnel rack:	
Crucibles, porcelain:	Coors No. 1a size.
Crucibles, platinum:	30 ml size.
Burette:	25 ml size.
Pipettes, volumetric:	
Filter paper:	Whatman No. 30 and No. 40, 9 cm dia.
Crucibles, filtering, Gooch high-form sintered glass:	30 ml size.

REAGENTS

Hydrochloric acid:	
Hydrochloric acid:	1:9 (v/v).
Hydrobromic acid:	
Hydrofluoric acid:	
Nitric acid:	
Nitric acid:	1:2 (v/v).
Nitric acid:	1:4 (v/v).
Sulphuric acid:	
Sulphuric acid, dil.:	1:1 (v/v).
Sulphuric acid, wash solution:	1:10 (v/v).
Sodium carbonate:	
Ammonium hydroxide:	
Ammonium hydroxide:	1:2 (v/v).
Alcohol, denatured:	
Ammonium carbonate:	saturated solution, freshly prepared
Hydrogen sulphide:	cylinder or lecture bottle

PROCEDURE

A. Preliminary Treatment

1. *For Solids*

Weigh a portion of the ore containing 2 to 25 mg of bismuth into a 250-ml beaker, add 25 ml of distilled water, 25 ml of concentrated hydrochloric acid and 5 ml of hydrobromic acid. If silica is high add 1 to 2 ml of hydrofluoric acid. Cover the beaker and heat to boiling. Boil for 15 to 20 minutes, partially remove the cover and evaporate nearly to dryness. Cool, cautiously add 8-10 ml of concentrated nitric acid and evaporate nearly to dryness. Add 10-15 ml of concentrated nitric acid and evaporate nearly to dryness. Add 10-15 ml of concentrated hydrochloric acid and boil for 10-15 minutes. A white curdy precipitate shows the presence of considerable silver.

(a) *Lead and Phosphates Absent*—Remove from the heat and add 15ml of 1:1 sulphuric acid. Heat to strong fumes. Do not evaporate to complete dryness. Wash down the sides of the beaker and heat again to strong fumes. Cool, add 25 ml of distilled water and boil gently for a few minutes. Cool quickly and filter through a No. 30 Whatman paper into a 400-ml beaker. Wash the residue with sulphuric acid wash solution. Wash the residue back into the original beaker, add 10 ml of 1:1 sulphuric acid and evaporate to strong fumes. Cool, add 25 ml of distilled water, digest for a few minutes, cool and filter through the same filter paper. Wash the residue with sulphuric acid wash solution.

(b) *Lead and Phosphates Present*—If large amounts of lead or phosphates are present, omit the sulphuric acid treatment and instead evaporate the solution twice to a small volume with 10-ml portions of concentrated hydrochloric acid to remove the nitric acid. Finally add 10 ml of concentrated hydrochloric acid and 25 ml of distilled water, heat to boiling and filter through a No. 30 Whatman filter paper into a 400-ml beaker. Wash the residue with 1:1 hydrochloric acid. Return the residue to the original beaker and digest with 10 ml of hydrochloric acid and 25 ml of water. Filter through the same filter paper and wash the residue with 1:1 hydrochloric acid.

Fuse the residue from the acid digestion with sodium carbonate. Spread the residue and filter paper out on a watch glass, dry and transfer as much of the residue as possible to a platinum crucible. Ash the filter paper in a porcelain crucible at as low a temperature as possible and transfer the ash to the platinum crucible. Add about 1-2 gm of sodium carbonate, mix and fuse. Digest the melt with distilled water, filter to remove phosphates and wash with hot distilled water. Discard this filtrate. Dissolve the residue in nitric acid, evaporate with either sulphuric or hydrochloric as above, dilute with water and filter into the beaker containing the filtrate from the first acid digestion.

2. *For Solutions*

Pipette an aliquot of the solution containing 2 to 25 mg of bismuth into a 400-ml beaker, add 10 ml of hydrochloric or sulphuric acid, dilute to 150 ml with distilled water, and proceed as for ores.

B. Hydrogen Sulphide Separations

Dilute the combined filtrates from one of the above methods of dissolution to about 150 ml with distilled water. Adjust the acidity to about 5 to 10% acid and saturate the solution with hydrogen sulphide to precipitate bismuth,

lead (not previously removed as a sulphate) copper, silver, etc. Filter through a No. 40 Whatman filter paper and wash the precipitate first with slightly acidified hydrogen sulphide water and then with a weak ammonium sulphide solution. Rinse the precipitate back into the beaker with distilled water, add 3-4 gm of potassium cyanide and heat to dissolve copper, silver, arsenic, antimony and tin sulphides. Filter through the same filter paper and wash the paper thoroughly with hot water. Wash most of the precipitate back into the original beaker with distilled water, place the beaker under the filtering funnel and wash the paper with warm 1:2 nitric acid. Spread out the filter paper if necessary and make sure all sulphides are washed into the beaker. Add 5 ml of concentrated nitric acid to the beaker and warm until all the bismuth is in solution and the separated sulphur is clean. Dilute to 25-30 ml with distilled water, filter into a 600-ml beaker and wash thoroughly with 1:2 nitric acid.

C. Precipitation

1. *As Bismuth Oxychloride*

Dilute the filtrate to about 250 ml with distilled water, heat to boiling and add dilute ammonium hydroxide (1:2) dropwise from a burette (with constant stirring) until a faint opalescence appears. If a precipitate forms, dissolve it by adding a few drops of dilute nitric acid (1:4) and repeat the neutralization. Add 5 ml of 1:9 hydrochloric acid, dilute the solution to about 450 ml with hot water, heat just to boiling and digest at a low heat for 2 to 3 hours or preferably overnight. Filter through a No. 40 Whatman filter paper and wash the paper and precipitate a few times with small amounts of hot water. Dissolve the precipitate with hot 1:9 hydrochloric acid by dropping the acid from a pipette around the edges of the filter paper, and catch the solution in the original beaker. Try to use about 4 ml of acid. Wash the paper with hot water, then with 1 ml of hot 1:9 hydrochloric acid and then again with hot water.

If 4 ml of 1:9 hydrochloric acid was used to dissolve the precipitate, dilute the solution to about 450 ml with hot water, bring just to a boil and digest for 1 to 2 hours at a low heat.

If more acid was required to dissolve the precipitate, dilute the solution to about 250 ml with hot water and neutralize with dilute 1:2 ammonium hydroxide until a faint opalescence appears. Add 5 ml of 1:9 hydrochloric acid, dilute to about 450 ml with hot water, and digest for 1 or 2 hours at a low heat.

Filter through a tared Gooch or sintered glass crucible, wash the precipitate with hot water and then with a little alcohol. Dry at 100°C, cool in a desiccator and weigh as BiOCl. Record the weight of the oxychloride. If the precipitate weighs more than 5 mg, proceed with "Precipitation as Bismuth Subcarbonate, etc." (which follows).

2. *As Bismuth Oxychloride, Alternative Procedure*

Evaporate the nitric acid solution of the sulphides just to dryness three times with 5-ml portions of concentrated hydrochloric acid. Wash down the sides of the beaker each time before adding the acid. During the last evaporation, tilt the beaker so the residue will collect in a small area. Add 5 ml of 1:9 hydrochloric acid and about 5 ml of distilled water. Heat until the salts are in solution, dilute to 450 ml with hot distilled water, digest and neutralize slightly if necessary. Bring just to a boil and digest 1 to 2 hours at a low heat. Filter through a previously tared sintered glass filtering crucible, and wash with hot water and alcohol. Dry at 100°C, cool and weigh as BiOCl. Record the weight. If more than 5 mg, proceed with the following.

3. *Precipitation as Bismuth Subcarbonate; and Weighing as Bismuth Oxide*

If the bismuth oxychloride precipitate from either of the above procedures weighs more than 5 mg, dissolve it in hot dilute 1:4 nitric acid and evaporate twice to a syrup consistency with the acid to remove chlorides. Dilute slightly and nearly neutralize the acid with dilute (1:2) ammonium hydroxide. Dilute to about 400 ml with hot water and add a slight excess of saturated ammonium carbonate solution. Heat to boiling and digest at a low temperature for 2 to 3 hours. Filter through a weighed Gooch crucible, dry and ignite at 1000°C to a constant weight. Record the weight of the precipitate as Bi_2O_3.

CALCULATIONS

For Solids

$$\% \text{ Bi} = \frac{\text{BiOCl} \times 0.8024 \times 100}{\text{wt. sample}}$$

$$\% \text{ Bi} = \frac{\text{Bi}_2\text{O}_3 \times 0.8970 \times 100}{\text{wt. sample}}$$

For Solutions

$$\text{gm/l Bi} = \frac{\text{BiOCl} \times 0.8024 \times 1000}{\text{aliquot taken}}$$

$$\text{gm/l Bi} = \frac{\text{Bi}_2\text{O}_3 \times 0.8970 \times 1000}{\text{aliquot taken}}$$

In any of the above cases, if the final weight of the precipitate obtained is less than 2 mg, the figure shall be reported as "less than" the limit of detection, an actual figure obtained by substituting the 2 mg figure in the appropriate equation above.

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MADE IN CANADA
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The Gravimetric Determination of Carbon Dioxide in Ores and Mill Products by Acid Evolution

METHOD C-1

SCOPE

This method is intended for use in the determination of carbon dioxide in carbonate-bearing ores.

RANGE

The method is suitable for the determination of carbon dioxide in the range 1 to 35% CO_2. Smaller amounts down to 0.1% can be determined with a lesser degree of accuracy.

OUTLINE

Carbon dioxide contained in such carbonate minerals as calcite, dolomite, magnesite, cerussite, witherite, strontianite, siderite, rhodochrosite, etc., is readily evolved when samples containing these minerals are boiled with hydrochloric acid.

$$MCO_3 + 2HCl \longrightarrow CO_2 + H_2O + MCl.$$

The bulk of the hydrochloric acid is returned to the reaction flask from the gas stream by a water-cooled reflux condenser. The evolved CO_2 is carried by a stream of purified air drawn through the apparatus by suction. The air stream is treated to remove all the other gases which are likely to interfere, and the CO_2 is absorbed in a weighed bottle containing soda-asbestos (ascarite) and a drying agent to absorb the moisture liberated by the sodium hydroxide-CO_2 reaction. The gain in weight of the bottle is a direct measure of the CO_2 in the sample taken.

$$2\ NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O.$$

Other acid gases (such as H_2S, AsH_3, Cl_2, HCl, SO_2) interfere since they are also absorbed and would be weighed.

Hydrochloric acid is used in spite of its volatility because most of its salts are soluble, so that no insoluble coating can form over the particles to slow down the reaction. Nitric acid is not used because it attacks a great many more sulphide minerals than does hydrochloric acid, liberating more H_2S, and its oxidizing action results in the formation of SO_2 and oxides of nitrogen which all interfere. Any traces of hydrochloric acid not absorbed by the other reagents are removed by a U-tube containing granular zinc.

The most common interference is hydrogen sulphide evolved by the reaction of the acid with metal sulphides, particularly pyrrhotite. Pyrite is reportedly not attacked by hydrochloric acid, but under the present conditions at least some hydrogen sulphide may be evolved.

$$Fe_7S_8 + 16\ HCl \longrightarrow 8\ H_2S + 5\ FeCl_2 + 2\ FeCl_3.$$

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Most of the hydrogen sulphide is removed by bubbling the evolved gases through an acidified saturated copper sulphate solution.

$$CuSO_4 + H_2S \longrightarrow CuS + H_2SO_4.$$

The balance is removed in a U-tube containing anhydrous copper sulphate absorbed on pumice.

Both arsenious chloride and arsine may be expected to be volatilized when ores containing arsenical minerals (arsenopyrite, rammelsbergite, etc) are boiled with hydrochloric acid. Presence of metals such as iron from grinding will promote the formation of more arsine.

$$Fe\,As_2 + 5\,HCl \longrightarrow FeCl_2 + AsCl_3 + AsH_3 + H_2.$$

The arsenic will be removed either in the copper sulphate solution:

$$2\,AsH_3 + 3\,CuSO_4 \longrightarrow Cu_3As_2 + 3\,H_2SO_4.$$

or by the manganese dioxide-asbestos mixture:

$$AsCl_3 + MnO_2 \longrightarrow AsOCl_3 + MnO.$$

$$AsH_3 + 4\,MnO_2 \longrightarrow H_3AsO_4 + 4MnO.$$

For ores high in arsenic and sulphur, the above treatment may be inadequate. In this case a washing bottle containing sulphuric acid saturated with chromic acid can be used to replace the one containing copper sulphate solution.

$$2\,CrO_3 + 3\,H_2SO_4 + 3\,AsCl_3 \longrightarrow 3\,AsOCl_3 + Cr_2(SO_4)_3 + 3\,H_2O.$$

$$AsH_3 + 2\,CrO_3 + 3\,H_2SO_4 \longrightarrow H_3AsO_3 + Cr_2(SO_4)_3 + 3\,H_2O.$$

It is most important that gas washing bottles provided with float valves (the type made by the Laboratory Equipment Corp., St. Joseph's, Michigan, Cat. No. 1055) be used with sulphuric acid, since, if the stopcock on the reaction flask is inadvertently closed while it is warm, and the sulphuric acid sucks back into the reaction flask containing hydrochloric acid, an explosion can result. Sulphur dioxide is not commonly evolved from ores, but it might be liberated from chemical products containing sulphites. It will be removed by the manganese dioxide-asbestos absorbent.

$$MnO_2 + SO_2 \longrightarrow MnSO_4.$$

If the only materials to be analyzed by this method are known to be free of arsenic and sulphur, the washing bottles containing chromic acid in sulphuric acid, copper sulphate solution and the U-tube containing manganese dioxide-asbestos can be eliminated.

Since the CO_2 weighing bottle absorbs moisture as well as CO_2, this also must be removed in advance. The concentrated sulphuric acid removes most of the water. The balance, including any developed by the other reactions, is removed first by calcium chloride then by magnesium perchlorate (a most vigorous drying agent).

It will be noticed that purified air drawn by suction is used to carry the evolved carbon dioxide through the train. This tends to reduce losses due to leaks and at the same time is considered safer than sweeping with gas under pressure. The gas washing bottles containing concentrated sulphuric acid solutions are provided with float-type check valves to prevent suck back and possible explosions. In the event of blockages in the system no attempt should be made to use pressure to clear them. SAFETY GLASSES MUST BE WORN WHEN ASSEMBLING OR DISMANTLING THE APPARATUS, when investigating faulty operation and when discarding solution. Caution must be used in cleaning out

the weighing bottle to avoid heat or caustic burns—do not add water to the bottle while holding it in the hand. Magnesium perchlorate can oxidize organic matter explosively and must be discarded in the sink under a flow of water.

APPARATUS

See Figure 1 for assembly

Drying tubes, U-shaped:	Fisher Scientific No. 9-240 (5 required).
Drying tube:	Fisher Scientific No. 9-215 (1 required).
Gas washing bottles:	Central Scientific No. 26213 or Fisher Scientific No. 3-030 (1 required).
Gas washing bottle:	with float valve, Leco No. 1055 (1 required).
Condenser:	Fisher Scientific No. 7-723-5 or 7-746.
Connecting tube:	Fisher Scientific No. 15-326B or 1 separatory funnel, Fisher Scientific No. 10-402.
Reaction flask:	250 or 300 ml flask, Fisher Scientific No. 10-047 or 10-060 or 10-044 (1 required).
Absorption bulb:	(CO_2) Nesbitt type, Fisher Scientific No. 7-517 (1 required).
Source of heat:	Gas burner (1 required).
Assortment of rubber stoppers:	
Assortment of rubber clamps:	
Analytical balance:	
Source of suction e.g. aspirator:	

REAGENTS

Pumice impregnated with copper sulphate:	Stir granular pumice (10-20 mesh) into a nearly saturated solution of copper sulphate. Allow the mixture to stand for a few hours, decant off most of the supernatant solution, dry, and store in a dry bottle.
Manganese dioxide-asbestos mixture:	Weigh 200 gm of $MnSO_4$. 4 H_2O into a 4-litre beaker or Erlenmeyer flask containing 2½ litres of water. When the salt dissolves add 50 gm of acid-washed asbestos (medium or long fibre), make distinctly ammoniacal with ammonium hydroxide, add 1 litre of freshly prepared ammonium persulphate (225 gm/l) and heat the mixture to boiling. Boil for 15-20 minutes adding ammonium hydroxide from time to time to keep the mixture ammoniacal. Allow the precipitate to settle for an hour or two and examine the supernatant solution. If the supernatant solution is cloudy, add another 100 ml of ammonium persulphate solution and boil for another 10 minutes with the addition of ammonium hydroxide as before. Allow the precipitate to settle, decant the supernatant solution and wash five times, by decantation, with 500 ml portions of hot water. Next wash thoroughly with water slightly acidified with sulphuric acid and finally again with hot water. Remove as much of the water as possible, spread out on a large shallow plate, dry and break up the mixture with a spatula. Store in a dry bottle.
Granulated zinc:	20 mesh.
Ascarite (soda asbestos):	8-20 and 20-30 mesh.
Anhydrone:	anhydrous magnesium perchlorate (or other suitable drying agent).

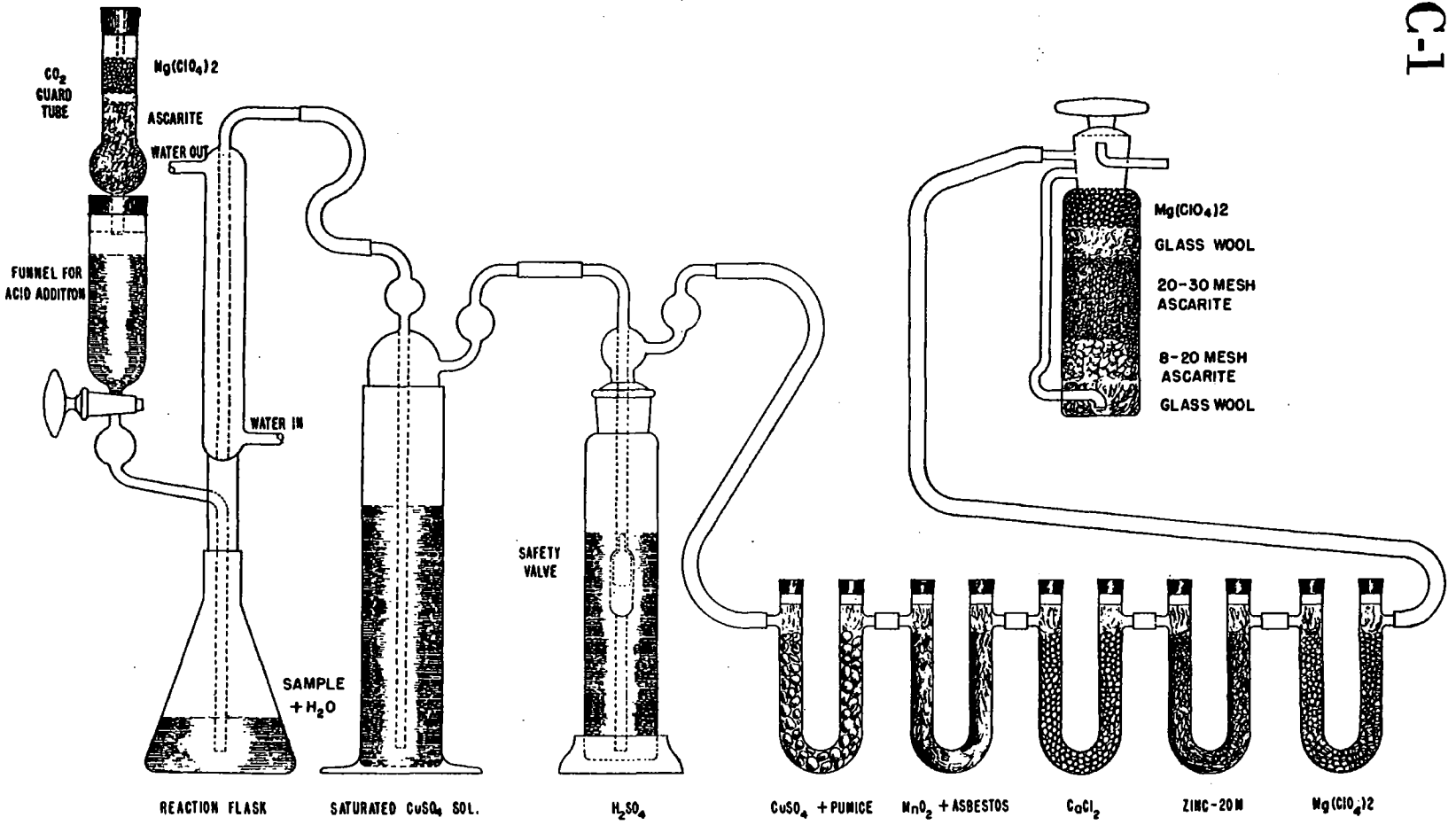

FIG. I - APPARATUS FOR DETERMINING CO_2 BY EVOLUTION

Sulphuric acid:
Hydrochloric acid:
Copper sulphate:
Pumice, ground: 10-20 mesh.
Asbestos: (medium or long fibre).
Ammonium persulphate:
Chromium oxide (CrO_3) or potassium or sodium chromate or dichromate:

Description of Purifying Train

The carbon dioxide is purified by passing it through the train shown in Figure 1.

In this train use is made of a condenser to condense most of the water, followed by (1) a washing bottle containing copper sulphate in 5% sulphuric acid or sulphuric acid saturated with chromium oxide* (CrO_3 or $Na_2Cr_2O_7$ etc.) to remove most of the hydrogen sulphide or sulphur dioxide from high sulphide ores etc., (2) a washing bottle containing concentrated sulphuric acid to bear the brunt of dehydration, (3) a tube filled with pumice impregnated with anhydrous copper sulphate to remove chlorine, hydrochloric acid, and hydrogen sulphide, (4) a tube filled with manganese dioxide-asbestos mixture to remove sulphur dioxide and hydrogen sulphide, (5) a drying tube filled with anhydrone or calcium chloride, (6) a tube filled with granulated zinc to remove chlorine etc., (7) a drying tube filled with anhydrone, (8) a CO_2 absorption tower filled with ascarite and anhydrone. Figure 1 also shows details of the filling of the CO_2 absorption tower.

PROCEDURE

Transfer 1-5 gm of the sample to the flask, cover the sample with water and connect it to the train. Insert the stopper containing the straight drying tube (filled with ascarite and anhydrone) in the connecting tube or separatory funnel, open the stopcock and draw air that is free from carbon dioxide through the system for 5-10 minutes. Close the stopcock in the connecting tube or separatory funnel, and connect a weighed CO_2 absorption tower to the train. For ores containing a large amount of carbon dioxide it is preferable to use two carbon dioxide absorption towers in the system. Remove the stopper containing the straight drying tube from the connecting tube or separatory funnel. Add 30 ml of 1:1 hydrochloric acid to the separatory funnel or connecting tube, replace the stopper containing the straight drying tube, open the stopcock and run acid into the flask slowly if there is much carbon dioxide, rapidly if there is but little. Draw air, free of carbon dioxide, through the system at a slow rate until effervescence diminishes, (5-10 minutes is usually sufficient). Check to see that water is flowing through the condenser and heat the flask slowly so as to obtain steady but quiet bubbling for 15-20 minutes. When it is judged that all the carbon dioxide has been boiled out of the solution, remove the source of heat, increase the current of air for 5-10 minutes to sweep out all the carbon dioxide, disconnect

* The use of sulphuric acid saturated with chromium oxide (CrO_3, $Na_2Cr_2O_7$ etc.) is preferable for arsenical ores.

the weighed CO_2 tower, close the inlet and outlet tubes and place in the balance case. When cool, open the stopcock momentarily, to equalize the pressure, and weigh using a tare weight as a counter-poise.

CALCULATIONS

$$\frac{\text{Increase in weight of the tower or towers} \times 100}{\text{Weight of sample}} = \%\ CO_2 \text{ in the sample.}$$

NOTE—If no weighable amount of carbon dioxide is obtained, report the result as less than the minimum amount detectable based on the sample weight taken. Assuming that such an amount is less than 2 milligrams, report

$$\%\ CO_2 = \text{less than } \frac{0.002 \times 100}{\text{Wt of sample taken}}$$

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2. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I.: Applied Inorganic Analysis, 2nd ed., New York, John Wiley and Sons Inc., 1953.
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The Rapid Determination of Total Carbon (including Carbonate) in Ores and Mill Products by the Combustion Method

METHOD C-2

SCOPE

This method is intended primarily for the rapid determination of carbonate in ores. Since it determines total carbon, the figure obtained will include graphite and organic carbon if these are present. If carbonate only is desired, a correction for them may be made by suitable modification of the method.

RANGE

A minimum of 0.15% CO_2 may be determined using a 1-gram sample. High percentages may be determined by reducing sample size.

OUTLINE

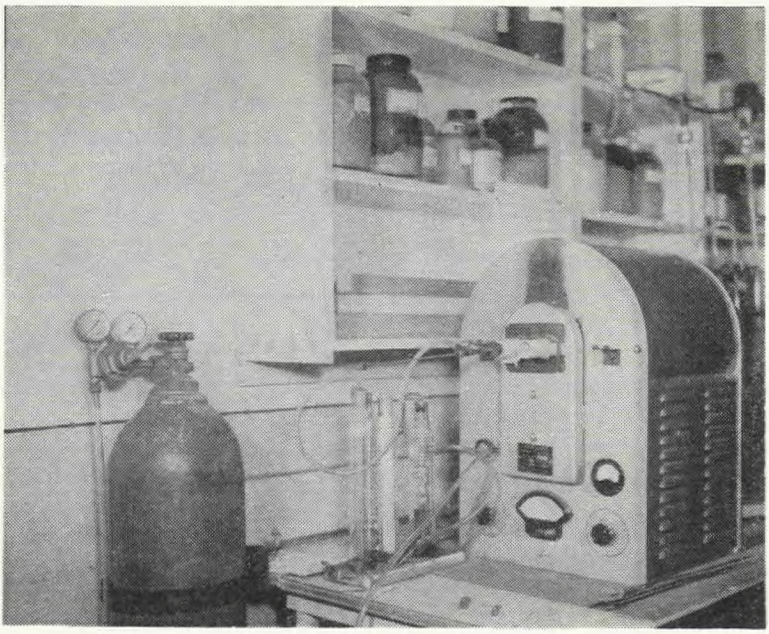
A weighed sample is heated in a combustion tube in a stream of purified oxygen at a temperature such that carbonates are decomposed into oxides and carbon dioxide, and carbon is oxidized. Sulphur is also oxidized. The gas stream passes through a sulphur trap which absorbs sulphur gases and into a carbon determinator which is a special type of gas burette (Figures 1A and 1B).

The carbon dioxide and oxygen are collected over a weak acid solution in this burette, a definite total volume being taken under standard conditions. This gas is then passed into a potassium hydroxide solution which absorbs the carbon dioxide. The oxygen is returned to the gas burette and the volume is again measured under the same standard conditions. The burette is so calibrated that the difference in volume is given directly as percent carbon in a 1.0- or 0.5-gram sample. For reporting, this value is converted to percent carbon dioxide (1).

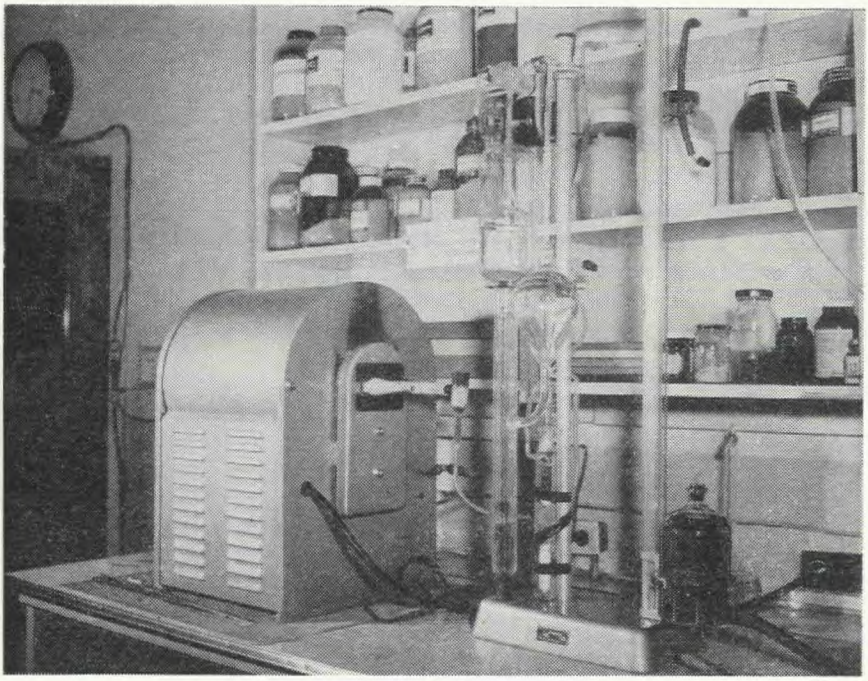
Interferences

Sulphur, nitrogen and halides interfere. A purifying tube containing manganese dioxide removes sulphur. Nitrogen and halogen compounds are not ordinarily encountered and the present method will not eliminate these interferences. The carbon in organic matter and in graphite is also measured, and a correction may be made for them by a separate determination (1, 4, 5) after acid treatment to remove carbonate.

Ordinarily, however, a determination by the evolution method will be more convenient (7).



A.



B.

FIG. 1—COMBUSTION APPARATUS FOR CARBON DETERMINATION. A. FRONT VIEW, SHOWING PURIFYING TRAIN. B. REAR VIEW, SHOWING SULPHUR TRAP AND TWO-MINUTE CARBON DETERMINATOR (LEVELLING BOTTLE AT LOWEST POSITION).

APPARATUS

See Figures 1A and 1B for photographs of complete set-up.

Combustion furnace:	Dietert No. 34410 (reference 3).
Combustion tube:	Dietert No. 3327-17, wide mouth.
Tube liners:	Dietert type F 2 No. 3057.
or	
Boat shields:	Dietert No. 3632.
Combustion boats:	Dietert No. 3031 type D (preignited several hours)
or	Leco Combax Size A.
Sulphur trap:	Dietert No. 3003-26.
Oxygen purifying train (including flow gauge):	Dietert No. 3004
or	Leco 1150.
Heat deflector:	Dietert No. 3452.
Boat pusher:	Dietert No. 3453.
Gas burette:	Dietert Two-minute.
Carbon determinator:	Dietert No. 3033.
Balance:	Accuracy of ± 0.05 mg is required.

REAGENTS

Sulphuric acid, concentrated:	(for purifying train)
Anhydrone:	(for purifying train)
Ascarite:	(for purifying train)
	Change above reagents every six months or if they appear to have deteriorated.
Manganese dioxide and glass wool:	(for sulphur trap) Refills—Dietert No. 3003-26a and b. Change every 3000 determinations, or oftener if high sulphur samples are being determined.
Metallic tin:	(accelerator) 30 mesh.
Oxygen:	Oxygen is supplied from the regular 200 cu ft cylinder equipped with a 2 stage reducing valve.
Potassium hydroxide solution:	820 gm KOH in 1200 ml water.
Sulphuric acid solution:	6 ml concentrated sulphuric acid to 1000 ml of water. Add 0.010 gm methyl orange and 5 ml wetting agent to the solution.

PROCEDURE

The apparatus is set up as described in the instruction booklets (2 and 3).

Table 1

Suggested sample weights	% CO_2
1.0 gm	up to 3%
0.5 gm	3%–25%
0.25 gm	25%–50%

Weigh an appropriate sample (*see* Table 1) into a combustion boat and cover with roughly twice as much metallic tin as sample by weight. A blank should be run before each series of samples, successive blanks being carried out

until a zero reading is obtained. The procedure for a blank determination is as follows:—

(1) Bring the furnace to 2600°F.

(2) Turn the valve handle on the five-way stockcock to the lower right-hand 45° position "4 o'clock". With the levelling bottle at its lowest point the burette reading should be zero. Raise the levelling bottle to the top position. As the liquid approaches the float valve, check its rise by pinching the tubing.

(3) Place the heat deflector stopper in the front end of the combustion tube. Turn the valve to the "6 o'clock" position. Lower the levelling bottle to the lowest position on the base.

(4) Turn on the oxygen at the furnace valve. When the liquid in the burette falls to within three-quarters of an inch of the zero mark, pull the heat deflector from the combustion tube and allow the burette to come to exactly zero. The oxygen is then shut off.

(5) Pass the gas in the burette into the absorption vessel by first moving the valve handle into the lower right-hand 45° position "4 o'clock". This subjects the absorption vessel to atmospheric pressure. Check the position of the movable marker at this time. Turn the valve to the "2 o'clock" position connecting the burette with the absorption vessel. Raise the levelling bottle to the top position thus causing the gas to bubble through the KOH.

(6) When the liquid in the burette rises to the burette float valve, lower the levelling bottle to the lowest position and allow the liquid to come to rest in the burette stem. Be cautious at this point to avoid flooding the five-way stopcock. Raise or lower the levelling bottle to cause the liquid in the absorption vessel to come in line on the marker, then take the reading of the bottom of the meniscus of the burette stem. Take the apparatus temperature reading when the liquid is at its highest point. The barometric pressure and room temperature are also required.

The procedure for samples is essentially the same as that for blanks.

(1) Turn the five-way valve to "4 o'clock" and raise the levelling bottle to fill the burette with liquid.

(2) Insert the sample boat into the hot zone of the tube and close the tube with the heat deflector, but do not turn on the oxygen.

(3) Turn the valve to "6 o'clock" and lower the levelling bottle. With no oxygen flowing, preheat the sample for 1-2 minutes.

(4) Open the oxygen valve and pass over gas until the liquid in the burette nearly reaches zero. Remove the heat deflector stopper and allow the burette to come exactly to zero. This step should be done over a period of at least 2 minutes. Continue as in procedure for blanks, steps (5) and (6).

Important: Graphite or Carbon Present

If the sample contains graphite and/or organic matter, this is determined separately on a second sample. Weigh out an appropriate sample (Table 1) into a 250-ml beaker and digest 30 minutes with 1:1 nitric acid on a steam bath. Transfer the sample quantitatively to a combustion boat and proceed as above.

If much graphite or organic matter is present, the carbonate should be determined by the evolution method, METHOD C-1.

CALCULATIONS

Barometric and ambient temperature readings are made, and the appropriate factor for converting the burette reading to normal temperature and pressure is found in Table 2.

Table 2

Factors for Conversion of Burette Reading to Volume at Normal Temperature and Pressure

Barometric pressure correction*

10 to 20°C subtract 2 mm. 30 to 32°C subtract 4 mm.
21 to 29°C subtract 3 mm. (To convert to value at 0°C)

Temperature in Degrees C	Volumetric Conversion Factors								
	Corrected Barometric Pressure (at 0° C)								
	730	*735*	*740*	*745*	*750*	*755*	*760*	*765*	*770*
18	0.951	0.958	0.964	0.971	0.978	0.985	0.991	0.997	1.004
19	0.946	0.954	0.960	0.969	0.973	0.980	0.986	0.993	1.000
20	0.942	0.949	0.955	0.961	0.968	0.975	0.982	0.988	0.995
21	0.937	0.944	0.950	0.957	0.964	0.971	0.977	0.983	0.990
22	0.932	0.940	0.946	0.953	0.959	0.965	0.972	0.978	0.985
23	0.928	0.935	0.941	0.948	0.954	0.961	0.967	0.973	0.980
24	0.923	0.930	0.936	0.943	0.949	0.956	0.962	0.968	0.975
25	0.918	0.925	0.931	0.937	0.944	0.951	0.957	0.963	0.970
26	0.913	0.920	0.926	0.933	0.939	0.945	0.952	0.958	0.965
27	0.908	0.915	0.921	0.927	0.934	0.940	0.947	0.953	0.960
28	0.903	0.909	0.916	0.922	0.929	0.935	0.942	0.948	0.955
29	0.898	0.904	0.911	0.917	0.924	0.930	0.936	0.943	0.949
30	0.893	0.899	0.905	0.911	0.918	0.924	0.931	0.937	0.944
31	0.887	0.894	0.900	0.906	0.913	0.919	0.926	0.932	0.938
32	0.882	0.888	0.895	0.901	0.907	0.914	0.920	0.926	0.933

* For mercury barometer only—aneroid barometer readings are already compensated.

The burette is calibrated in percent carbon and has two scales corresponding to 1.0- and 0.5-gram samples. If another sample size is taken this must be allowed for. All results are expressed as CO_2.

$$\% \, CO_2 = \text{Bur. Rdg.} \times \text{Conv. Factor} \times 3.67 \times \frac{\text{scale (1.0 or 0.5)}}{\text{sample wt. gm}}$$

If no appreciable change in volume occurs on absorbing the CO_2, the result should be expressed as "less than" the limit of detection. Since the burette cannot be read more closely than 0.02% carbon, this figure may be calculated as follows:—

$$\% \, CO_2 = \text{less than } 0.04 \times \text{Conv. Factor} \times 3.67 \times \frac{\text{scale (1.0 or 0.5)}}{\text{sample wt. gm}}$$

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2. Dietert Instruction Booklet for Varitemp Combustion Furnace, Nov. 15, 1950.
3. Dietert Instruction Booklet for Two Minute Carbon Determinator No. 3003, January 5, 1951.
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5. Hillebrand, W. F., and Lundell, G. E. F.: Applied Inorganic Analysis, New York, John Wiley and Sons, 1929.
6. Methods of Analysis of Iron and Steel, *Mines Br., Ottawa.*, Feb. 1950.
7. Method C-1.

The Volumetric Oxalate Method for Calcium

METHOD Ca-1

SCOPE

The method is applicable to all materials containing calcium in sufficient quantities to be determined volumetrically. If strontium is present it will be precipitated as the oxalate and subsequently titrated and reported as calcium oxide. Provision is also made for a gravimetric finish if desired.

RANGE

From 0.0005 gm to 0.1 gm of calcium oxide can be determined in the following method. Larger amounts can be determined by diluting a solution of the sample to a known volume and using an aliquot, or by weighing the ignited oxides.

OUTLINE

Dissolution of the sample depends upon the type of material being analyzed. Ores containing phosphates, fluorides or sulphates and/or large amounts of silica, are fused with a mixture of sodium carbonate and potassium nitrate. The cooled melt is digested with water containing a little hydrogen peroxide and filtered to remove the above interfering elements. The residue is dissolved in hydrochloric acid. Samples containing sulphides and arsenides are dissolved in acids, filtered, and the residue fused and treated as above. Members of the hydrogen sulphide group, such as lead and copper, are removed by precipitating them from an acid solution with hydrogen sulphide. Aluminum, iron, and titanium are either removed by precipitating them twice with ammonium hydroxide, if they are present in large amounts, or by complexing them with tartaric acid if they are present in small amounts. Cobalt, manganese and nickel, are removed by precipitating them with ammonium sulphide. Finally, calcium is separated from magnesium and most of the barium, by precipitating it from a slightly acidic solution with either ammonium oxalate or oxalic acid. The calcium oxalate is either titrated with standard potassium permanganate or ignited and weighed.

$$5\,Ca(COO)_2 + 2KMnO_4 + 8\,H_2SO_4 \longrightarrow 5\,CaSO_4 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 10\,CO_2.$$

APPARATUS

Gas burner, Meker:	
Hot plate:	
Balance, analytical:	
Crucibles, platinum:	25 or 30 ml size.
Tripod:	
Triangles:	silica covered.

Beakers, Griffin:	250, 400, 600, 800 ml sizes.
Beakers, Berzelius:	300, 400 ml sizes.
Beaker covers, Speedyvap:	
Beaker covers, watch glass form:	
Crucible tongs, platinum tipped:	
Beaker tongs:	
Filter paper:	Whatman No. 41H, 30, 42.
Funnels, Bunsen long stem:	65 and 75 mm dia.
Burettes:	50 ml size.
Pipettes, volumetric:	5, 10, 25, 50 ml sizes.
Flasks, volumetric:	250, 500 ml sizes.
Bottles, washing:	1 litre size.
Bottles, reagent:	
Bottles, dropping:	
Crucibles, filtering, Gooch high form, fritted glass:	medium porosity 30 ml size.
Flasks, filtering, suction:	500 ml size.

REAGENTS

Sodium carbonate:	
Potassium nitrate:	
Oxalic acid:	
Ammonium oxalate:	
Potassium permanganate:	
Nitric acid:	
Hydrochloric acid:	
Perchloric acid:	
Hydrogen sulphide:	lecture bottle or cylinder.
Ammonium hydroxide:	
Sodium sulphite:	
Hydrogen peroxide, 30%:	
Ammonium chloride:	
Sodium hydroxide:	
Hydrogen sulphide wash solution, acid:	1% v/v hydrochloric acid, saturated with hydrogen sulphide.
Methyl red indicator solution:	Dissolve 0.02 gm of the indicator in 100 ml of hot water, let the solution cool, and filter.
Ammonium sulphide solution:	Saturate ammonium hydroxide solution (1:9), with hydrogen sulphide.
Ammonium sulphide wash solution:	Add 10 ml of ammonium sulphide solution to 1 litre of water containing 10 gm of ammonium chloride and a few drops of ammonium hydroxide.

Silica—pure, fine:	
Calcium carbonate:	
Standard calcium solution, 1 ml = 1 mg CaO:	Dissolve 1.79 gm of calcium carbonate in as little hydrochloric acid as possible and dilute to 1 litre. Take 20 ml aliquots and standardize by precipitating with ammonium oxalate and titrating with 0.1N potassium permanganate.
Tartaric acid:	
Hydrobromic acid:	
Bromine:	
Bromine water:	A saturated solution of bromine in distilled water.
Standard potassium permanganate solution, 0.1N:	Dissolve 3.161 gm of potassium permanganate in 1 litre of freshly boiled and cooled distilled water. Let stand a few days and filter through glass wool or a sintered glass crucible into a dark bottle. 1 ml = 0.0028 gm CaO. Standardize the permanganate against pure sodium oxalate as outlined below.
Standard potassium permanganate solution, 0.05N:	Dissolve 1.58 gm of potassium permanganate in distilled water in the same way as for the 0.1N solution, 1 ml = 0.0014 gm CaO.
Sodium oxalate, U.S. National Bureau of Standards:	

Standardization of Potassium Permanganate Against Sodium Oxalate

Dry National Bureau of Standards sodium oxalate at 110°C for 1-2 hours. For the stronger permanganate solution, weigh 0.240 gm of the dried sodium oxalate into a 250-ml beaker. Add 150 ml of distilled water and 10 ml of 1:1 sulphuric acid. Heat to 80-90°C (do not boil) and then titrate with the potassium permanganate, with stirring, to the first permanent pink colour. The colour should last for 1-2 minutes. For the weaker permanganate, use 0.120 gm of sodium oxalate. During the first part of the titration, the permanganate may be added at the rate of 10 ml per minute. Near the end-point it should be added dropwise. The temperature of the solution should not be below 60°C at the end of the titration.

0.240 gm $Na_2C_2O_4$ = 0.1004 gm CaO.

0.120 gm $Na_2C_2O_4$ = 0.0502 gm CaO.

Calculate the grams of CaO per ml of permanganate.

For the strong permanganate: $1 \text{ ml} = \frac{0.1004}{T} \text{ gm CaO} = f_1$.

For the weaker permanganate: $1 \text{ ml} = \frac{0.0502}{T} \text{ gm CaO} = f_2$

where T = the permanganate titration in ml.

PROCEDURES

A. General Procedure

1. *Preliminary Treatment*

(a) *Solid Samples, Acid Decomposition*—Weigh a portion of the sample, preferably containing 0.005 to 0.05 gm of calcium, into a 250-ml beaker. Add 20 ml of hydrochloric acid, 20 ml of water and 5-10 ml of hydrobromic acid. Heat to boiling and boil for 20-30 minutes. If the arsenic or antimony contents are high, repeat the hydrochloric-hydrobromic treatment. Cautiously add 5-10 ml of nitric acid and boil until the excess bromine is expelled. Add 8-10 ml of perchloric acid, and, if the sample is high in fluorides and low in silica, add a few milligrams of fine pure silica. Evaporate the solution to heavy fumes, cover the beaker and reflux for 15-20 minutes. Cool, wash down the sides of the beaker with distilled water, dilute to 30-40 ml with distilled water and digest until the soluble salts are in solution. Filter through a No. 30 Whatman filter paper and wash the paper and residue thoroughly with distilled water. Reserve the filtrate. If the fluoride content is negligible or if the silica content is high, dehydration of the silica can be accomplished by evaporating the solution to dryness with hydrochloric acid instead of refluxing with perchloric acid. Transfer the paper and residue to a platinum crucible, dry, char and ignite the filter paper. Fuse the residue with about six or seven times its weight of sodium carbonate. Transfer the cooled melt to the original beaker, add 50-60 ml of water and digest on the hot plate until the mass is thoroughly disintegrated. Filter through a Whatman No. 30 paper and wash the paper and residue thoroughly with a hot 5 percent sodium carbonate solution. Discard the filtrate and washings. Place the beaker containing the reserve filtrate under the funnel and dissolve the residue from the paper with a little hot 1:1 hydrochloric acid. Wash the paper with hot water.

(b) *Solid Samples, Fusion Decomposition, for Ores, Precipitates and Other Solid Samples Containing Phosphates, Sulphates, Fluorides and/or Large Amounts of Silica (Arsenides, Sulphides or Easily Reducible Metals Absent or Present in Negligible Quantities)*—Weigh a sample, preferably containing 0.005 to 0.05 gm of calcium oxide, into a platinum crucible. Add about eight to ten times as much sodium carbonate as ore, mix thoroughly, cover with a little sodium carbonate and 0.5 gm of potassium nitrate. Fuse over a Meker burner until a clear melt is obtained. Cool, transfer the crucible and melt to a 400-ml beaker containing 200-250 ml of distilled water and 4-5 ml of hydrogen peroxide. Digest on the hot plate, until the mass is thoroughly disintegrated, and filter through a No. 30 Whatman filter paper. Wash the paper and residue with a hot 5 percent sodium carbonate solution. Discard the filtrate and washings. Wash most of the precipitate back into the beaker with distilled water. Place the beaker under the funnel and dissolve any residue remaining on the paper with 5-10 ml of 1:1 hydrochloric acid. Wash the paper with hot water. Add additional hydrochloric acid to the solution in the beaker, and digest on the hot plate to take up all the soluble material. If any undecomposed residue remains, filter through a No. 30 Whatman paper into a clean beaker, and wash the paper and residue with hot water. Reserve the filtrate and washings. Transfer the paper and residue to a platinum crucible. Dry, char, and burn off the filter paper. Fuse the residue with about six times its weight of sodium carbonate, cool, transfer the cooled melt to a 400-ml beaker containing 200-250 ml of water and 3-4 ml of 3 percent hydrogen peroxide. Digest on the hot plate, until the mass is thoroughly disintegrated, filter through a No. 30 Whatman filter paper and wash with a hot 5 percent sodium carbonate wash solution. Discard the filtrate and washings. Place the beaker containing the reserve filtrate under the funnel and dissolve any residue in the precipitation

beaker with hot 1:1 hydrochloric acid. Pour the acid through the filter paper until all soluble material is dissolved and finally wash the beaker and paper with hot water. Discard the residue on the paper. Dilute the combined filtrates to 100-150 ml.

(c) *Solutions*—Pipette an aliquot portion of the solution into a 400-ml Berzelius beaker. Add 10 ml of nitric acid and evaporate to dryness. Digest the residue with 10 ml of nitric acid, add 8-10 ml of perchloric acid and evaporate to heavy fumes. Cover the beaker and reflux for 10-15 minutes. Cool, dilute to 50 ml with distilled water, digest until the soluble salts are in solution and filter through a No. 30 Whatman filter paper into a clean 250-ml beaker. Wash the paper and residue with hot water and discard the paper and residue. Dilute the filtrate to 100-150 ml.

If interfering ions are present in large amounts, carry through the appropriate separations below.

If interfering ions are low in concentration or are absent, add 1 gm of tartaric acid and complete the determination by the rapid procedure ("B").

2. *Carbonate Separation*

If the phosphate content is high, nearly neutralize the solution with sodium hydroxide. Add 3-4 gm of sodium carbonate and 3-4 ml of 3 percent hydrogen peroxide. Digest on the hot plate for 15-20 minutes to coagulate the precipitate. Cool, let settle, and filter through a No. 30 Whatman filter paper. Wash the paper and residue with a hot 5 percent sodium carbonate solution. Discard the filtrate and washings. Wash most of the precipitate back into the beaker, place the beaker under the funnel and dissolve any precipitate remaining on the paper with hot 1:1 hydrochloric acid. Wash the paper with hot water. Discard the filter paper. Dissolve any undissolved precipitate in the beaker with a little hydrochloric acid and add 4-5 ml in excess.

If the phosphate content is low or if the iron and titanium content greatly exceeds the phosphate, omit the above separation. Neutralize the solution with ammonium hydroxide, acidify with hydrochloric acid and add 4-5 ml excess.

3. *Hydrogen Sulphide Separation*

Dilute the solution to 100-150 ml, add 0.5 to 1 gm of sodium sulphite, heat to boiling and boil until the excess sulphur dioxide is expelled. Pass hydrogen sulphide through the solution for 15-20 minutes. Cool, filter through a No. 42 Whatman filter paper into a 400-ml beaker and wash the paper and precipitate with an acidulated hydrogen sulphide solution (10 ml of hydrochloric acid in 1 litre of water saturated with hydrogen sulphide). Do not let the paper or precipitate become dry during filtration or washing. Discard the paper and residue unless copper is being determined on the same portion of the sample. Heat the filtrate to boiling and boil until the excess hydrogen sulphide is expelled. Add 2-3 ml of bromine water and boil until the excess bromine is expelled. Dilute to 200 ml.

4. *Ammonia Separation*

Add 2 gm of ammonium chloride, a few drops of methyl red indicator solution and enough ferric chloride to combine with all the phosphate present. Neutralize the solution with 1:1 ammonium hydroxide plus a 1-ml excess and

boil for 3-4 minutes. Filter through a No. 41H Whatman paper. Wash the precipitate with a hot 2 percent solution of ammonium chloride. Reserve the filtrate. Dissolve the precipitate in 1:1 hydrochloric acid, dilute to 150-200 ml, add 2 gm of ammonium chloride and a few drops of methyl red indicator and reprecipitate the iron, titanium, etc., with ammonium hydroxide as outlined above. Filter and wash the precipitate as before and combine the filtrates. Discard the residue.

5. *Ammonium Sulphide Separation*

If such elements as manganese, nickel and cobalt are present, bubble hydrogen sulphide through the filtrate for 10-15 minutes and filter through a No. 42 Whatman filter paper into a clean beaker. Wash the paper and precipitate with the ammonium sulphide wash solution. Neutralize the filtrate from either the ammonium hydroxide or ammonium sulphide separation with hydrochloric acid and boil to expel any excess hydrogen sulphide. Add 5-6 ml of bromine water and evaporate to 150-200 ml. Filter, if necessary, into a clean beaker; wash the paper with a hot 1 percent hydrochloric acid solution. Discard the paper and residue. Dilute the filtrate to 200-250 ml.

6. *Oxalate Precipitation*

If the magnesium content is high, add (by means of pipette) 10 ml of the standard calcium oxide solution, 2-3 drops of methyl red indicator and 15-20 ml of a saturated oxalic acid solution. If the magnesium content is low, omit the addition of the standard calcium oxide. Heat the solution to just below boiling and then slowly add 1:1 ammonium hydroxide, with stirring, until the solution is just alkaline (i.e. just turns yellow). Add 5 gm of ammonium oxalate and heat just below boiling for 20-30 minutes. Allow the solution to cool for 1 hour and filter through a No. 42 Whatman filter paper. Wash the precipitate a few times with a cool 0.1 percent solution of ammonium oxalate. Reserve the filtrate for the determination of magnesium. Dissolve the washed oxalate precipitate in 15-20 ml of hot 1:1 hydrochloric acid and dilute to 150-200 ml. Add 2-3 drops of methyl red, 5-10 ml of saturated oxalic acid solution, 1 gm of tartaric acid, and heat just below boiling. Slowly add 1:1 ammonium hydroxide until the solution is just alkaline. Add 3 gm of ammonium oxalate, and digest on the hot plate for 15-20 minutes. Cool for 1 hour and filter through a No. 42 Whatman filter paper. Wash the paper and precipitate three to four times with a cool 0.1 percent ammonium oxalate solution and then five to six times with hot water to remove excess ammonium oxalate. Combine the filtrate and washings with the reserve filtrate for the determination of magnesium, if this assay is required; otherwise discard it.

7. *Final Treatment*

(a) *Gravimetric Finish*—Transfer the precipitate to a tared platinum crucible, dry and ignite the paper carefully over a burner. Transfer to a muffle furnace, ignite at 1000°C for 1 hour, cool in a good desiccator with fresh desiccant, and weigh as CaO. Record the weight.

(b) *Volumetric Finish*—Wash most of the precipitate back into the precipitation beaker with hot water, place the beaker under the funnel and dissolve any precipitate remaining on the paper with 10-15 ml of warm 1:1 sulphuric acid. Wash the paper with hot water. Make sure all the precipitate in the beaker dissolves, dilute to 100-150 ml with distilled water and heat to 70-80°C. Do not boil. Titrate the *hot* solution with standard potassium permanganate to the first permanent pink. Add the filter paper and continue the titration to the first permanent pink colour. The colour should last for at least 1 minute (at not less than 60°C). Record the titration in ml (T).

B. Rapid Routine Procedure for Dolomitic Limestones and Brucite (Phosphate, Fluorides, and Sulphates Absent) (4)

Weigh 0.2000 to 0.5000 gm of sample into a 400-ml Berzelius beaker, moisten with 5 ml of water and add 10 ml of perchloric acid. Digest on the hot plate to fumes of perchloric acid, cover with a watch glass and heat until the acid refluxes freely for 10-15 minutes. Remove from the hot plate and cool. Cautiously add 50-60 ml of hot water and digest on the hot plate until the soluble salts are in solution. Filter through a No. 30 Whatman filter paper into a 250-ml beaker. Wash the paper and residue with hot water. Discard the paper and residue unless silica is being determined. Evaporate the filtrate to about 60 ml. Add 1 gm of tartaric acid, 10 ml of the standard calcium oxide solution (if magnesium is high) and 3-4 drops of methyl red. Cool to room temperature and neutralize to the methyl red end-point with 1:1 ammonium hydroxide. Dilute to 100 ml, add 15 gm of ammonium oxalate crystals, stir a little and heat to boiling. Boil for 1 minute and filter immediately through a sintered glass crucible using suction. Wash the precipitate six to eight times with small portions of hot water. Reserve the filtrate for the determination of magnesium. Dissolve the precipitate in warm 1:1 sulphuric acid. Dilute to 100 ml with distilled water, heat to 80-90°C and titrate with 0.1N potassium permanganate as before. Record the titration in ml (T).

CALCULATIONS

Gravimetric finish:

Solids

$$\% \text{ CaO} = \frac{\text{wt CaO}}{\text{sample wt. gm}} \times 100$$

Solutions

$$\text{gm/l CaO} = \frac{\text{wt CaO}}{\text{sample vol., ml}} \times 1000$$

Volumetric finish:

Solids

$$\% \text{ CaO} = \frac{(\text{T f} - \text{CaO added})}{\text{sample wt., gm}} \times 100$$

Solutions

$$\text{gm/l CaO} = \frac{(\text{T f} - \text{CaO added})}{\text{sample vol., ml.}} \times 1000$$

where T = permanganate titration, ml

f = factor, gm CaO per ml for the permanganate used.

If the sample titration has a value approximately equivalent to the calcium oxide added, the amount of CaO should be reported as less than the minimum amount detectable (an actual figure based on the sample weight or volume used). Assuming the minimum amount detectable with the weaker permanganate standard is 0.0005 gm, then the figure to report may be calculated on this basis; for example:

$$\% \text{ CaO} = \text{less than } \frac{0.0005 \times 100}{\text{wt. sample}}$$

$$\text{gm/l CaO} = \text{less than } \frac{0.0005 \times 1000}{\text{aliquot taken}}$$

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The Turbidimetric and Gravimetric Determination of Chloride in Uranium Concentrates

METHOD Cl-1

SCOPE

This method is intended for the determination of chloride in uranium concentrates for specification purposes.

RANGE

The turbidimetric modification will detect as little as 0.001% Cl. Chloride above 0.15% is determined gravimetrically.

OUTLINE

Chloride is determined by adding silver nitrate to the nitric acid solution of the sample and comparing the turbidity produced with that of standards. In larger amounts the silver chloride is precipitated by boiling, filtered off and weighed.

Silver chloride has a solubility of 1.4 mg/l at room temperature, but this is very much reduced if nitric acid and excess silver nitrate are present. Anions which give silver salts insoluble in nitric acid are also covered by this method. These include bromide, iodide, thiocyanate, sulphide, thiosulphate, ferrocyanide and ferricyanide. Fluoride is not precipitated, however.

Where excess chlorate is used in the sulphuric acid leach process, some of the chlorate reports in the uranium concentrate, especially if the amine solvent extraction method of up-grading is employed. Unless the chlorate is reduced, chloride present in this form will not be included by the method outlined. Reduction can be accomplished by treatment with a saturated solution of sulphur dioxide, or by a preliminary fusion of the sample with sodium carbonate.

Uranium does not interfere. Chromate, phosphate, arsenate, oxalate, and carbonate may also be present without interfering. Chromium and mercury if present may tie up chloride and prevent its precipitation. Tin and antimony may hydrolyze in the weakly acid solution and their hydroxides would then be counted as chloride. In general these interferences are not anticipated in the concentrate and are not removed.

Silver chloride is light sensitive and decomposes in strong light. The light of fluorescent lamps is particularly active in this respect. In consequence, all operations with the precipitate should be carried out in diffuse incandescent light.

APPARATUS

Beakers, Pyrex, Griffin, low form:	50 ml and 250 ml sizes.
Watch glasses:	to fit above.
Nessler tubes:	50 ml size, set of 12.
Funnels, filtering, Bunsen long stem:	
Crucibles, filtering, sintered glass:	fine porosity 30 ml cap.
Filtering flask, Buchner, with tubulature:	250 ml size.
Adapter for filtering crucibles:	to hold crucibles in flask.
Analytical balance:	
Dark cupboard:	to store solutions during precipitation.
Steam bath:	
Oven:	110° C.
Crucible, platinum:	30 ml size.

REAGENTS

Standard chloride solution:	Dissolve 0.0165 gm NaCl in water and dilute to 1 litre. 1 ml = 0.01 mg Cl.
Silver nitrate solution 0.1N:	1.7 gm $AgNO_3$ in 100 ml water.
Silver nitrate wash solution:	2 ml of the above solution diluted to 1 litre.
Nitric acid concentrated:	
Nitric acid, dil., 1:1:	v/v.
Nitric acid 0.01N:	Dilute 0.32 ml nitric acid to 500 ml.
Orange oxide:	UO_3, halogen-free.
Sodium carbonate:	anhydrous.

PROCEDURE

Turbidimetric Procedure (Chlorate Absent)

Weigh a 1.00-gm sample and five 1.00-gm portions of halogen-free orange oxide (UO_3) and transfer each into a 50-ml beaker. Pipette 1, 2, 3, 4 and 5 ml, respectively, of the standard chloride solution (0.01 mg Cl per ml) into the five samples of orange oxide. Add 8 ml of dilute nitric acid (1:1 v/v) to each sample and to the standards. Cover and digest on the steam bath till dissolved. Wash down the cover and the sides of the beaker. Filter each solution through a Whatman No. 42 filter paper into a 50-ml Nessler tube, washing with water until each filtrate is almost 50 ml in volume. Add 1 ml of 0.1 N silver nitrate solution to each and dilute to volume with water. Mix and visually compare the turbidity of the sample solution with that of each of the standards. Record the chloride content of the sample as the amount present in the standard it most closely resembles, and calculate the % Cl on this basis.

If the amount so calculated is close to the specification limit, carry out the gravimetric procedure below.

Gravimetric Procedure (Chlorate Absent)

Weigh a 2.00-gm sample into a 250-ml beaker. Moisten with water, then add 100 ml water and 5 ml nitric acid. Warm on the steam bath for 30 minutes, stirring to dissolve. Filter through a Whatman No. 42 filter paper into a clean 250-ml beaker and wash the residue with 1% nitric acid. Cool the filtrate, and add 20 ml of 0.1N silver nitrate with constant stirring. Heat the solution to boiling and stir, to coagulate the silver chloride precipitate. Test for complete precipitation after the precipitate has settled by adding a drop or two more of the silver nitrate and noting if there is any cloudiness in the clear supernatant solution. If there is, add more silver nitrate and boil again. Let the solution stand for 30 minutes or longer (preferably overnight) in a dark place and decant the clear solution through a tared sintered glass crucible, using suction. Wash the precipitate by decantation with silver nitrate wash solution. Transfer all of the precipitate to the crucible, wash well with 0.01N nitric acid until the precipitate is free of silver (test the filtrate with a few drops of hydrochloric acid), then wash with water. Dry the crucible and its contents in the dark at 110°C to constant weight and record the weight of silver chloride obtained.

Gravimetric Procedure (Chlorate Present)

Weigh a 2.00-gm sample into a 30-ml platinum crucible, add 10 gm anhydrous sodium carbonate and mix well. Heat over a Meker burner using a low flame at first, then increase the temperature gradually until complete fusion has been obtained, using the full heat of the flame. Cool and transfer the melt to a 250-ml beaker. Dissolve in water, at the same time cautiously neutralizing with nitric acid, using methyl red indicator, and make to 100 ml. Boil to expel CO_2, cool, add 5 ml of nitric acid and carry out the balance of the procedure as outlined above.

CALCULATIONS

Turbidimetric procedure

$$\% \text{ Cl} = \frac{\text{chloride in standard closest to sample} \times 100}{1.0}$$

Gravimetric procedure

$$\% \text{ Cl} = \frac{\text{wt. AgCl} \times 0.2474 \times 100}{\text{wt. sample}}$$

The Volumetric Determination of Chloride

METHOD Cl-2

SCOPE

This method, which actually determines all of the halogens except fluoride, can be used for the determination of the chloride content of uranium precipitates for specification purposes, for the analysis of brines and ion exchange eluates, and for the analysis of leach liquors.

RANGE

The method as outlined will detect as little as 0.03% total halogens as chloride in the precipitates, and 0.003 gm/l total halogens in solution.

OUTLINE

The halogens (except fluoride) are precipitated as the silver halides, using a slight excess of standard silver nitrate solution. This excess is then titrated with a standard solution of potassium thiocyanate. Thiocyanate, like chloride, forms a slightly soluble silver compound in acid medium, and an excess of thiocyanate is readily detected by its sensitive reaction with ferric iron (1). This end-point ordinarily has a tendency to fade due to the presence of the silver chloride precipitate, which reacts with the excess thiocyanate (since silver thiocyanate is less soluble than silver chloride). The addition of a small amount of nitrobenzene before the back-titration obviates this difficulty by preferentially coating the silver chloride and shielding it from the thiocyanate ions. (2).

Strong oxidizers (for example chlorine and hydrogen peroxide in concentrations greater than 0.005 M) interfere by oxidizing the thiocyanate to produce reddish or yellowish colours. Trivalent thallium and the lower oxides of nitrogen also decompose thiocyanate and must be removed. Very strong nitric acid is also detrimental.

Mercury and palladium form complexes with thiocyanate and must be absent. If sulphide, sulphite or thiosulphate are present, the solution, acidified with nitric acid, should be boiled until these compounds have been volatilized or oxidized.

None of the above compounds are removed in the method described since they are not commonly found in the materials analyzed. Their interference should be borne in mind.

Uranium interferes by virtue of its yellow colour, which obscures the end-point. It is removed by a double ammonia precipitation.

Alternatively, cation exchange may be used, but a description of the step is not included in the procedure given.

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The mercurimetric procedure for chloride, given in METHOD A.X.-1, may also be used for the same purposes as this procedure. Uranium interferes with it also, due to the high uranium/chloride ratio, so the same separations would apply.

APPARATUS

Beakers, Griffin low form:	250 ml size.
Flasks, Erlenmeyer:	500 ml size.
Funnels, filtering, Buchner:	9 mm dia.
Flasks, filtering, suction:	500 ml size.
Filter paper:	Whatman No. 40, 9 cm dia.
Burettes:	25 and 50 ml sizes.

REAGENTS

Nitric acid, concentrated:	
Nitric acid, dil.:	1:1 v/v.
Ammonium hydroxide:	fresh.
Ferric alum indicator:	40% ferric alum in water.
Nitrobenzene:	
Standard silver nitrate solution, 0.1N:	Dissolve 8.495 gm $AgNO_3$ in water and dilute accurately to 500 ml.
Standard potassium thiocyanate solution 0.1N:	Dry the salt in a vacuum desiccator, then in an oven at 140° C. Dissolve 4.856 gm in water and dilute accurately to 500 ml.
Standard potassium chloride solution, 1 ml = 0.0030 mg Cl:	Dry pure KCl at 100° C for 2 hours. Dissolve 1.8773 gm in water and dilute accurately to 500 ml.

Standardizations of Solutions

For most work it will be satisfactory to assume that the solutions as prepared above are of the strengths noted. If necessary standardize the silver nitrate by precipitating the silver as chloride and weighing it (*see* METHOD Cl-1). The other solutions can be standardized against the silver nitrate.

PROCEDURE

A. Sample Preparation

1. *Solid Samples*

Weigh a suitable sample (containing at least 2.5 mg Cl) into a 250-ml beaker. Dissolve in a minimum of concentrated nitric acid (about 5 ml). Dilute to 100 ml. Cover the beaker and boil 2-3 minutes. Remove the beaker from the hot plate, let cool slightly and add a small excess of fresh ammonium hydroxide with vigorous stirring. Cover the beaker and boil 1 minute. Transfer the slurry to a Buchner funnel and filter using suction. Wash with about 150 ml hot water in 50-ml portions, letting the wash drop to the surface of the cake, but not allowing the cake to crack until all the washing is completed. Transfer the filtrate to a 500-ml Erlenmeyer flask. Transfer the precipitate to a 250-ml beaker, dissolve in nitric acid, and reprecipitate and wash as before. Combine the filtrates.

2. *Solution Samples*

For barren eluates, take a suitable aliquot of the sample (containing about 25 mg Cl). For samples containing uranium, carry out a preliminary separation as described under "Solid Samples". In all cases, transfer the uranium-free solution, containing 2.5 to 25 mg Cl, to a 500-ml Erlenmeyer flask.

B. Titration Procedure

Add 20 ml dil nitric acid (1:1) to the contents of the flask. Add standard 0.1N silver nitrate from a burette until there is a 10-15% excess (e.g. 3-5 ml on a 30-ml titration). Add about 5 ml of nitrobenzene (1 ml for each 0.05 gm chloride), stopper, and shake vigorously until the precipitate is coagulated and coated with nitrobenzene.

Add 1 ml of ferric alum indicator and titrate the residual silver nitrate with 0.1N potassium thiocyanate until a permanent faint reddish brown colouration appears. Record the volume of silver nitrate taken and the volume of the thiocyanate titration.

CALCULATIONS

$$\% \text{ Cl} = \frac{(N_a V_a - N_b V_b)}{\text{Sample weight}} \times 0.0355 \times 100$$

$$\text{gm/l Cl} = \frac{(N_a V_a - N_b V_b)}{\text{Sample volume}} \times 0.0355 \times 1000$$

where N_a = normality of silver nitrate solution
N_b = normality of potassium thiocyanate solution
V_a = Volume of silver nitrate solution taken, ml
V_b = Titration of potassium thiocyanate, ml.

References

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The Colorimetric Determination of Cobalt in Ores and Solutions

METHOD Co-1

SCOPE

This method is intended for the determination of cobalt in ores, products and solutions (5, 6).

RANGE

The lower limit is about 0.05% or 0.05 gm/l, based on 2.0 gm or 25-ml sample with a dilution of 10 ml for the final colour development, using 1-cm cells for reading the colour.

OUTLINE

Ammonium thiocyanate produces with cobalt a blue complex $(NH_4)_2Co(SCN)_4$ (1) which can be extracted with certain organic solvents (2, 3). The cobalt concentration of the extracted cobalt thiocyanate complex is then measured spectrophotometrically at its maximum (in the visible region) at 610 mμ (4) or at 570 mμ for larger amounts. It might be noted that the extracted complex absorbs very strongly at 312 mμ but at this wave length iron interference is quite serious (4). The relationship between the intensity of the cobalt complex and the cobalt content of the extract is not linear but follows a curve of wide radius. It is possible to determine with reproducible results amounts of cobalt up to 4.0 mg, by reading the colour intensity of the cobalt complex in a spectrophotometer against a suitable blank (at the less sensitive wave length of 570 mμ in 1-cm cells).

An excess of thiocyanate over that required to form the complex is necessary to permit its extraction. Even then, the distribution coefficient, E_a^o, is only about 10 (i.e. only 80% is extracted by 5 ml of solvent from 25 ml of aqueous phase) (2). In rapid work, this incomplete extraction is corrected by using a calibration curve based on standards prepared in the same way. In accurate work, sufficient extractions must be carried out to ensure quantitative recovery, to guard against errors caused by slight variations in distribution from analysis to analysis. In the present case, three extractions will give 99.2% recovery. Four are used as a safeguard.

Chromium, manganese, nickel, zinc, titanium, molybdenum and copper do not give coloured complexes which are soluble in amyl alcohol and ether. Silica, aluminium, calcium, magnesium, phosphorus, bismuth, arsenic, lead and the alkalies have no effect.

Ferric iron constitutes a serious interference in spite of the fact that its thiocyanate complex is not very soluble in ether-containing solvent mixtures.

Its effect is overcome by reducing it with a mixture of sodium thiosulphate and sodium phosphate. Ferrous iron can be tolerated in concentrations up to about 40% of the sample. Above this amount, ammonium acetate and tartaric acid can be used to eliminate its effect. This same technique can be used to eliminate the interference due to vanadium which otherwise would give a similar blue complex which is also extracted by amyl alcohol-ether.

The optimum pH for extraction is about 3.5 and an adequate distribution is obtained between pH 2.8 and 4.0. This is maintained by use of ammonium acetate buffer.

The concentration of reagents is very important so all reagent solutions should be added by burette or pipette. For the lower range, where a single extraction is used and the volume of the extract is not adjusted, the solvent too, should be added by pipette. In particular, the thiocyanate concentration must be above 24% for optimum colour development and extractability. The formation constant of the complex is low and as can be seen from its formula, the concentration of the complex varies as the fourth power of thiocyanate concentration, so that this must be maintained accurately. The colour is not too stable and must be read within one-half hour after its development.

APPARATUS

Beakers, Griffin low form:	100 ml and 250 ml sizes.
Beaker covers, watch glass:	
Cylinders, graduated:	10 ml size.
Funnels, filtering, Bunsen long stem:	65 mm dia.
Flasks, volumetric:	250, 100 and 50 ml sizes.
Pipettes, volumetric:	5, 10 and 25 ml sizes.
Bulbs, rubber, pipetting:	
Funnels separatory, Squibb pear shape:	
Funnel racks:	Single and double types.
Burettes:	50 ml and 10 ml.
Spectrophotometer:	
Spectrophotometer cells:	1 cm and 5 cm sizes.

REAGENTS

Hydrochloric acid:	
Nitric acid:	
Perchloric acid:	
Ammonium hydroxide, dil:	1:1, v/v.
Sodium phosphate—sodium thiosulphate solution:	125 gm $Na_2S_2O_3$. 5 H_2O and 31.25 gm Na_3PO_4 . 12 H_2O in 1 litre of water.
Ammonium thiocyanate solution:	600 gm of NH_4SCN in 1 litre of water.
Ammonium acetate solution:	700 gm of $NH_4(CH_3COO)$ in 1 litre of water.
Tartaric acid solution:	50 gm of tartaric acid in 100 ml of water.

Isoamyl alcohol-ether mixture: 3 parts by volume of isoamyl alcohol with 1 part of diethyl ether.

Standard cobalt solution: Dissolve 2.5 gm high purity cobalt metal in dilute hydrochloric acid and dilute to 500 ml in a volumetric flask —1ml = 5 mg Co. Transfer aliquots containing 0.5 to 35 mg Co to 100 ml beakers, and dilute to 25 ml. Neutralize with dil. ammonium hydroxide solution and make just acid with dil. hydrochloric acid solution. Add 1 ml concentrated hydrochloric acid, transfer to a 50 ml volumetric flask and dilute to volume. This will provide solutions such that 5 ml will contain 0.05 to 3.50 mg Co.

Preparation of the Calibration Graph

(a) *For Small Amounts of Cobalt (less than 0.35 mg).*

Single Extraction Method—To five 60-ml separatory funnels, add by pipette or burette 10 ml ammonium thiocyanate solution, 8 ml sodium phosphate-sodium thiosulphate solution and 4 drops (0.15 ml) tartaric acid solution. Shake well. To these add 5 ml of standard cobalt solutions containing 0.05, 0.10, 0.15, 0.20 and 0.35 mg Co. Mix well and add by pipette, using a rubber bulb, 10 ml of isoamyl alcohol-ether. Shake the separatory funnel for about 30 seconds. Run off the bottom (aqueous) layer and let a few drops of the organic layer follow it to wash aqueous solution out of the stem. Finally run the organic phase into spectrophotometer cells (1-cm and 5-cm light path) and read against a blank of distilled water at 610 mμ. Plot a curve of cobalt in mg Co per 10 ml extract as abscissae, against optical density as ordinates.

(b) *For Large Amounts of Cobalt (0.35 to 3.5 mg Co)*

Multiple Extraction Method—Follow above procedure using standard cobalt solutions containing 0.50, 0.75, 1.5, 2.5 and 3.5 mg Co, up to the point where the solvent is added to the funnel. Carry out four successive extractions with 10-ml portions of the solvent mixture, using a graduated cylinder to add the solvent and drawing the aqueous layer into a second separatory funnel for the successive extractions. Filter the extracts successively into a 50-ml volumetric flask (to remove water), and rinse the paper with a few ml of solvent. Make to volume with solvent, mix well, and read at 570 mμ in 1-cm cells (and in 5-cm cells at 610 mμ) against water. Plot calibration curves of mg Co per 50 ml as abscissae against optical density as ordinates for the 1-cm and 5-cm cells.

PROCEDURE

A. Initial Treatment

1. *Solid Samples*

Weigh a suitable portion (Table 1) of the sample into a 250-ml beaker. Add 10 ml concentrated hydrochloric acid, cover and heat for 10 minutes. Add 5 ml nitric acid and heat another 10 minutes. Add 5 ml perchloric acid, leave the cover off and evaporate to strong fumes, but do not bake. Take up with water, add a few ml hydrochloric acid and filter into a clean beaker. Wash the paper well, and discard the residue. Neutralize the filtrate with dil. ammonium hydroxide, make just acid with dil. hydrochloric acid and add 1 ml concentrated hydrochloric acid for each 50 ml of final dilution. Transfer to a volumetric flask of appropriate size (Table 1) and dilute to the mark.

2. *Solution Samples*

Transfer a suitable aliquot of the solution (Table 2) to a 250-ml beaker. Add 25 ml water, then neutralize with dil. ammonium hydroxide. Add 1 ml concentrated hydrochloric acid for each 50 ml of final dilution. Transfer to a volumetric flask of appropriate size (Table 2) and dilute to the mark.

B. Colour Development

1. *Rapid (Single Extraction) Method, For Small Amounts of Cobalt (Less than 0.35 mg).*

To 60-ml separatory funnels add by pipette or burette 10 ml of ammonium thiocyanate solution, 8 ml of sodium phosphate-thiosulphate solution, 2 ml of ammonium acetate solution and 4 drops (0.15 ml) of tartaric acid solution. Shake well. Add the 5-ml aliquot of the sample solution, (diluted to contain not more than 0.35 mg Co). Add by pipette (use a rubber bulb), 10 ml isoamyl alcohol-ether mixture. Stopper the funnel and shake for about 30 seconds. Run off the bottom (aqueous) layer, followed by a few drops of the organic layer to rinse the aqueous phase out of the stem. Run the organic extract into a 1-cm cell and read against a water blank using a wave length of 610 mμ. Determine the cobalt content as mg Co per 10 ml volume from the previously prepared calibration graph and record this result.

2. *Accurate (Multiple Extraction) Method for Cobalt in the Range 0.35 to 3.5 mg Co.*

Proceed as in above method up to the point where the solvent is to be added, but using 5-ml aliquots containing correspondingly larger amounts of cobalt. Carry out 4 successive extractions with 10-ml portions of the solvent mixture using a graduated cylinder to add the solvent and drawing the aqueous layer into a second separatory funnel for the successive extractions. Filter the extracts successively through the same paper into a 50-ml volumetric flask, finally washing the paper with a few ml of solvent. Make to volume with solvent, mix well and read at 570 mμ in 1-cm cells (or if an accurate estimation of small amounts is needed, at 610 mμ in 5-cm cells). Determine the cobalt content as mg Co per 50 ml volume from the previously prepared calibration graph and record this result.

Table 1

Dilution Table for Solid Samples

Range %	Sample wt. gm	Dilute to ml	Take Aliquot, ml
0.05–1.0	2	100	5
1.0 –2.0	1	250	5
2.0 –4.0	1	500	5

Table 2

Dilution Table for Solution Samples

Range gm/l	Sample volume ml	Dilute to ml	Take ml
0.05–1.0	25	100	5
1.0 –2.0	10	250	5
2.0 –4.0	10	250	5

CALCULATIONS

$$\% \text{ Co} = \frac{\text{mg Co (from graph)}}{1000 \times \text{sample wt. gm}} \times \frac{\text{final dilution}}{\text{aliquot taken}} \times 100$$

$$\text{gm/l Co} = \frac{\text{mg Co (from graph)}}{1000 \times \text{sample vol. ml}} \times \frac{\text{final dilution}}{\text{aliquot taken}} \times 1000$$

If no significant reading is obtained report the result as "less than" the minimum amount detectable, an actual figure based on the sample weights and aliquots used, rather than using the term "not detected". The minimum amount detectable using the single extraction technique may be taken as 0.035 mg. The figure to report in such a case would be for example:

$$\% \text{ Co} = \text{less than } \frac{0.035}{1000 \times \text{sample wt. gm}} \times \frac{\text{final dilution}}{\text{aliquot taken}} \times 100$$

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The Determination of Bicarbonate, Carbonate and Hydroxide in Alkali Carbonate Leach Liquors and Process Solutions

METHOD CO_3-1

SCOPE

Methods are given for the determination of bicarbonate, carbonate and hydroxide in the solutions used in the alkali carbonate processes for the recovery of uranium from its ores (1, 2), and in other carbonate process solutions, such as strip solutions from solvent extraction processes.

RANGE

The smallest amount of bicarbonate that can be detected by the method given is 0.5 gm/l $NaHCO_3$, the lower limit for carbonate is 0.1 gm/l Na_2CO_3, and for hydroxide 0.2 gm/l NaOH.

OUTLINE

The methods described below are based on the potentiometric titration of the ionic species sought, using standard acid or base solution of known strength.

If a solution containing sodium hydroxide and sodium carbonate is titrated with standard acid solution, the following reactions occur:—

$NaOH + H^+ \longrightarrow Na^+ + H_2O$ (end-point pH 10 to 4) (Equation 1)

$Na_2CO_3 + H^+ \longrightarrow Na^+ + HCO_3^-$ (end-point pH 8.2) (Equation 2)

followed by

$NaHCO_3 + H^+ \longrightarrow Na^+ + H_2CO_3$ (end-point pH 4.0) (Equation 3)

and

$H_2CO_3 \longrightarrow H_2O + CO_2$ (Equation 4)

In titrating a solution of sodium bicarbonate with standard hydroxide solution, the reaction occurring is given by

$NaOH + NaHCO_3 \longrightarrow Na_2CO_3 + H_2O$ (end-point pH 11.3) (Equation 5)

From these equations it is apparent that if the pH of the solution as received is above 11.3, hydroxide ion is present, and carbonate may be present, but bicarbonate is absent. If the pH is in the range 8.2 to 11.3, carbonate and bicarbonate may be present, but hydroxide is absent. If the pH is in the range 4.1 to 8.2, the bicarbonate ion only is present (unless uranium is also present—*see* below). If the pH is less than 3.2 none of the three ions (OH^-, CO_3^{2-}, HCO_3^-) is present (less than pH 4.1 if uranium and thorium are absent).

Carbonate solutions from the leaching of uranium ores and from solvent extraction processes contain a number of ions which interfere with the direct

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determination of hydroxide, carbonate and bicarbonate with acid. The principal impurity, sulphate ion, arising either from solution and oxidation of sulphide in the ore, or from the sulphate in sulphuric acid leach liquors which is absorbed by the solvent and stripped by carbonate, may occur in concentrations exceeding those of all other ions, if the carbonate solution is being recycled (1). It does not interfere directly in the procedures described, but may cause a shift in the end-points of the various titrations (6), so that these should be checked from time to time by plotting the titration curves to a point well beyond the inflection of the curves. It will also of course interfere in the procedure for determining hydroxide "Procedure C", section 2 unless additional barium chloride solution is added to make the solution at least 0.1 N in barium ions.

Other impurities that may be present are arsenate, phosphate, silicate, vanadate, and, of course, uranium and thorium.

In the presence of uranium, some of the carbonate ion is tied up by the reaction

$$UO_2^{++} + 3CO_3^{2-} \rightleftharpoons UO_2(CO_3)_3^{4-} \qquad \text{(Equation 6)}$$

The carbonate ion contained in this complex is not titrated by acid up to pH 8.2. It is titrated, along with bicarbonate, from pH 8.2 to pH 4.0 (except that as the uranium content increases, the pH of the second end-point is progressively lowered, e.g. to pH 3.2 for 2 gm U_3O_8/l (4, 5, 7). Figure 1 illustrates the extent of this lowering as a function of the uranium content of the solution, and can be used in choosing the proper end-point for the determination, if acid titration is to be employed.

The change in the pH of the second end-point results from hydrolysis of some of the uranyl ion. This ion, liberated from the complex by destruction of the bicarbonate, finds itself in a medium whose hydroxyl ion content is still too high for it to exist entirely in the unhydrolyzed form. The hydrolysis reaction, as postulated by Sutton, (8, 9) takes the form

$$2UO_2^{++} + H_2O \rightleftharpoons U_2O_5^{++} + 2H^+ \qquad \text{(Equation 7)}$$

(At a pH of 4.2, Sutton shows that as much as half of the uranium is present as the $U_2O_5^{++}$ ion).

Consequently, the titration of the uncomplexed bicarbonate is followed without any break by the titration of the carbonate in the complex, but part of this titration follows the path

$$2UO_2(CO_3)_3^{4-} + 10\,HCl \longrightarrow U_2O_5^{++} + 6CO_2 + 5H_2O + 10\,Cl^- \qquad \text{(Equation 8)}$$

This completed, the hydrogen ion content begins to increase, causing a barely perceptible inflection, which is then followed by the titration of that portion of the uranium in the hydrolyzed form.

$$U_2O_5^{++} + 2HCl \longrightarrow 2UO_2^{++} + H_2O + 2Cl^- \qquad \text{(Equation 9)}$$

The overall reaction corresponds stoichiometrically to the sum of Equations 3 and 10

$$UO_2(CO_3)_3^{4-} + 6\,HCl \longrightarrow UO_2^{++} + 6Cl^- + 3CO_2 + 3H_2O \qquad \text{(Equation 10)}$$

As a result of the series of reactions involving the uranyl carbonate complex, however, the final end-point is displaced to lower pH values than it has in the absence of uranium. If the titration is carried out arbitrarily to pH 4.0 and if the solution carries a high concentration of uranium values, the result can be considerably in error. This can be overcome either by plotting the titration

curve and establishing the end-point of the final reaction graphically; or by carefully standardizing the pH indicating apparatus and using the corrected end-point pH given in Figure 1.

Bicarbonate is therefore determined by titration with sodium hydroxide (Equation 5) as described in Procedure A, since the uranium complex does not interfere in this determination (4). If the amount of sample available is small however, the bicarbonate may be titrated with acid in the usual way, and the bicarbonate result corrected for the amount of uranium complex which is titrated at the same time. One gm U_3O_8 is equivalent to 1.796 gm $NaHCO_3$ in this titration and the corrected bicarbonate content is thus given by

$$\text{gm/l } NaHCO_3 \text{ (true)} = \text{gm/l } NaHCO_3 \text{ found} - (1.796 \times \text{gm/l } U_3O_8).$$

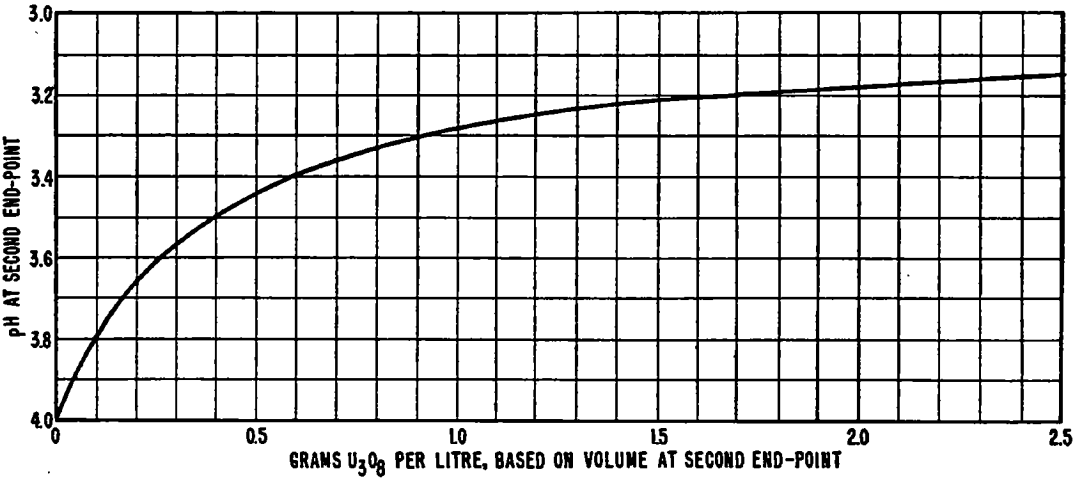

FIG. 1—EFFECT OF URANIUM CONCENTRATION ON pH OF SECOND-END POINT (PROCEDURE D)

Carbonate, in the absence (Procedure B) and in the presence (Procedure C 1) of hydroxide ion, is determined according to Equation 2, by titration to pH 8.2. As we have noted, the presence of uranium does not interfere in this titration. It should be remembered, however, that there *is* carbonate ion tied up by uranium which is not accounted for by these titrations. The amount so complexed, which can be calculated from Equation 6 (5), is 1.133 gm Na_2CO_3 per gm of U_3O_8.

The situation with regard to thorium is, in general, similar to that for uranium. That is, some of the carbonate is tied up in a complex which appears to have the composition $Th(CO_3)_5^{6-}$.

Once again, the carbonate tied up in the complex is not titrated by acid up to the first inflection (pH 8.2 to 7.9). It is titrated, following the titration of the uncomplexed bicarbonate, with no intervening inflection. In this case, however, the thorium liberated from the complex is quantitatively precipitated as the hydroxide, due to the insolubility of thorium hydroxide at the pH existing in the solution at this point. As a result, there is a second clearly defined

end-point which occurs at pH 4.5 to 4.1 and which corresponds stoichiometrically to the sum of Equation 3 and the following reaction:

$$Th(CO_3)_5^{6-} + 6\ HCl \longrightarrow Th(OH)_4 + 6\ Cl^- + 5CO_2 + H_2O$$ (Equation 11)

A third sharp end-point, marking the end of the re-solution reaction of the acid on the precipitated thorium hydroxide, follows the second end-point at a pH of 3.5 to 3.2:

$$Th(OH)_4 + 4HCl \longrightarrow ThCl_4 + H_2O$$ (Equation 12)

The true bicarbonate content can, once again, be determined by titration with sodium hydroxide (Equation 5) as in Procedure A, but the end-point, while well-defined, is displaced and occurs at pH 10.8 to 11.0. Indeed if the titration is continued to pH 11.5 as for solutions containing uranium, much of the thorium precipitates, breaking up the complex and consuming hydroxide (16). A second inflection is found at pH 11.7 to 12.1, which corresponds stoichiometrically to the reaction:

$$Th(CO_3)_5^{6-} + 4\ OH^- \longrightarrow Th(OH)_4 + 5\ CO_3^{2-}$$ (Equation 13)

A precipitate corresponding to the formula $ThCO_3(OH)_2$ may separate at an intermediate pH.

If the amount of sample is small, Procedure D can be employed and a rough estimate of the true bicarbonate content obtained by correcting for the titration of the complex. The correction is made by subtracting 1.910 gm/l $NaHCO_3$ for each gm/l ThO_2 contained in the sample.

If Procedures A and B were employed to determine carbonate and bicarbonate, it must once more be borne in mind that the carbonate which has not been titrated, is tied up in the thorium complex, and corresponds to 2.007 gm Na_2CO_3 per gm ThO_2 present (16).

Thus the methods outlined for uranium-containing solutions appear completely applicable to thorium-containing solutions. However, since the inflection points for the various reactions in the presence of thorium are not as clear cut as for uranium, the titrations should be carried out on the recording titrator and the end-points determined from the recorded curves.

Hydroxide can be determined in two ways. An aliquot of the solution can be titrated with standard acid, first to pH 8.2 giving the sum of the titrations of the hydroxide and carbonate contents in the solution, according to Equations 1 and 2. The bicarbonate formed from the carbonate ion according to Equation 2 can be titrated with more acid according to Equation 3 to pH 4.1. Since this second titration is exactly equivalent to the carbonate originally present, it can be subtracted from the first titration (carbonate plus hydroxide) to give the hydroxide content of the solution. This method could be used since if hydroxide ion is fairly high, most of the interfering uranium has probably been precipitated. However, the hydroxide content of these solutions (usually barren carbonate solutions after uranium precipitation) is usually low (1-4 gm/l), and the combined small errors of the two titrations result in a serious error in the hydroxide determination. Furthermore, the lower the hydroxide content, the greater the amount of uranium left in the solution, and the more serious the error from this source.

For these reasons, hydroxide ion is determined by Winkler's method (6, 10) (Procedure C 2). An excess of 10% barium chloride solution is added, precipitating the carbonate according to the reaction:

$$BaCl_2 + Na_2CO_3 \longrightarrow Ba_2CO_3 + 2\ NaCl$$ (Equation 14)

If sulphate is present, sufficient barium chloride must be added to leave the solution 0.1N in barium ion. The hydroxide is then titrated with hydrochloric acid to the equivalence point, which in this solution has been found experimentally to be pH 9.2 (6).

If the carbonate content is also desired, another aliquot is titrated with the same acid to pH 8.2, giving the combined hydroxide and carbonate contents (Procedure C 1) and the carbonate content is obtained by subtracting the hydroxide content determined by Procedure C 2.

INTERFERENCES

Since the presence of uranium and thorium, governed the choice of methods used, their interferences have already been discussed. The other interferences mentioned occur less frequently.

Phosphate and arsenate constitute practically identical interferences. In Procedure A (titration of bicarbonate with sodium hydroxide), if the starting pH is between 4.3 and 9.5, phosphate will be present as H_2PO_4 and will be titrated according to:

$$H_2PO_4 + NaOH \longrightarrow Na^+ + HPO_4^{2-} + H_2O \text{ (end-point pH 9.5)} \qquad \text{(Equation 15)}$$

In addition, the presence of phosphate flattens the curve making the bicarbonate-carbonate end-point at pH 11.3 (Equation 5) quite flat and difficult to detect. The stoichiometry of the reaction to this end-point is correct, however, so that provided the measuring system is carefully standardized, no error will result. The titration can be corrected by calculating the phosphate content in terms of ml of 2N NaOH, and subtracting this from the titration obtained for the bicarbonate content. The phosphorus content can be determined by the regular colorimetric procedure. The correction is then given by:

$$\frac{1000 \times \text{gm } P_2O_5 \text{ in the aliquot taken}}{71 \times \text{N of NaOH}} = \text{ml titration equivalent to phosphorus present.}$$

Another difficulty which may arise in the titration of bicarbonate in solutions with high uranium concentration is hydrolysis of the uranium. This is easily overcome by adding sufficient bicarbonate-free carbonate solution to dissolve the precipitated uranium.

Phosphorus and arsenic also interfere in the titration of carbonate using acid (Procedures B and C). Since the titration is just carried to pH 8.2, the only reaction that need be considered is:

$$PO_4^{3-} + H^+ \longrightarrow HPO_4^{2-} \text{ (end point pH 9.5)} \qquad \text{(Equation 16)}$$

and

$$AsO_4^{3-} + H^+ \longrightarrow HAsO_4^{2-} \text{ (end-point pH 8.2)} \qquad \text{(Equation 17)}$$

Once again the simplest procedure is to calculate the phosphate and arsenate content in terms of ml of 0.2N acid and to subtract this from the titration obtained for the carbonate content (3), the phosphorus and arsenic contents being determined by the regular colorimetric procedure (11).

For phosphate, the equivalent volume of 0.2N acid is given by

$$\frac{1000 \times \text{gm } P_2O_5 \text{ in the aliquot taken}}{71 \times 0.2}$$

and for arsenate by

$$\frac{1000 \times \text{gm As in the aliquot taken}}{75 \times 0.2}$$

Thus if a titration of 24.3 ml is obtained from a 10-ml aliquot of carbonate solution containing 1 gm/l P_2O_5, the true carbonate content can be determined by subtracting

$$\frac{1000 \times 0.01}{71 \times 0.2} = 0.7 \text{ ml}$$

from 24.3 ml. The carbonate content is therefore

$$\frac{23.6 \times 106 \times 0.2}{1000 \times 10} = 50 \text{ gm/l}$$

The factors for As and P_2O_5 are sufficiently similar that the combined As + P_2O_5 figure will be accurate enough for these corrections.

It is not necessary to correct the sodium hydroxide figure (Procedure C 2) since phosphate and arsenate are undoubtedly precipitated by the barium chloride.

Silica probably interferes with the carbonate titration according to the reactions:

$$Na_2SiO_3 + H_2O \longrightarrow 2\ NaOH + SiO_2 \qquad \text{(Equation 18)}$$

$$2\ NaOH + 2HCl \longrightarrow 2\ NaCl + 2\ H_2O \qquad \text{(Equation 19)}$$

and the equivalent volume of 0.2N HCl would be given by:

$$\frac{1000 \times \text{gm } SiO_2 \text{ in the aliquot taken}}{30 \times 0.2}$$

Correction for vanadium has not been investigated.

The application of these corrections is not given under "Calculations" as ordinarily they are considered beyond the scope of the method.

The analyst must be aware of them, however, since inevitably if a balance of the various ions cannot be obtained, the analysis is questioned. If any of the interfering ions is present in significant amounts, it is possible that the discrepancy may arise from that fact. The fact that some of the carbonate is tied up in the uranium complex, which is not titrated by the methods given, must also be taken into account.

APPARATUS

Precision Dow Recordomatic Titrator: Carefully read the instruction manuals (12), (13), before attempting to turn on the unit. Check to make sure the titrator has had its regular oiling. If the unit is used for caustic solution, be sure to remove all caustic solutions from the delivery unit at the end of the day's work.

Beckman Autotitrator: This instrument, with two delivery units, is well suited to the routine analysis of a large number of solutions. One side is used for the 0.2N hydrochloric acid, the other for the 2.0N sodium hydroxide. Carefully read the instruction manual (14) before using. Remove the top of the delivery units and check the rubber valve diaphragms at regular intervals, especially before using. Replace the rubber diaphragm if it shows signs of attack. Keep the glass stopcocks of the burettes closed, and clamp off the connections from the stock bottles to the gravity-filled burettes, to prevent leakage of solution into the delivery unit. Other automatic titrators are probably satisfactory for this analysis.

Beckman Model C or Model H2 pH meter: These or any other suitable pH meters may be used for these determinations, especially if only a small number of analyses are required. Carefully read the instruction manuals (15) before using. Always check and adjust with fresh buffer solution in the range being used. The model H2 instrument is more convenient to use, but the adjustment of the meter needle to the indicator needle setting (switch at "Standby") must be made regularly especially when the instrument is warming up.

Glass electrode: Blue glass (high pH) type.

Saturated calomel electrode: sleeve type.

Pipettes: 5, 10, 25, 50 and 100 ml.

Beakers: 250-ml or 400-ml Griffin or Berzelius types, as required for the instrument used.

REAGENTS

Standard hydrochloric acid, 0.2N: Dilute 135 ml of concentrated (12 M) C.P. hydrochloric acid to 8 litres. Store in an aspirator bottle connected to the gravity-filled burette of the Autotitrator. Standardize against pure sodium carbonate as follows:

Weigh accurately 0.4-gm portions of pure dry sodium carbonate into three 250-ml beakers, dissolve in about 100 ml of distilled water and titrate with the acid to a pH of 4.2.
Calculate the normality from the formula

$$N = \frac{\text{wt. of } Na_2CO_3 \times 1000}{53 \times \text{titration (ml)}}$$

Sodium hydroxide, 2.0N: Weigh 680 gm C.P. sodium hydroxide into a beaker and cautiously dissolve in about 1 litre of water (mechanically stirred) contained in a 2- or 3-litre beaker. Do not add more sodium hydroxide at one time than will dissolve in a reasonable time, and take care that the solution does not become so hot as to boil. (Keep the solid caustic in a 32-oz. screw cap bottle while preparing the solution, and do not keep the top off longer than necessary.) *This solution is dangerously caustic and must be handled carefully.* When all the caustic has been dissolved and the solution is cool, filter through glass wool (to remove carbonate, which does not dissolve at this concentration) into a 6-gal. polyethylene aspirator bottle and dilute to 8 litres. Connect the bottle to the gravity-filled burette.
WARNING: Do not leave this solution standing in any of the burettes when not titrating.

Standardize the solution by the following procedure:

Weigh 10-gm portions of potassium acid phthalate accurately (by difference) into two 250-ml beakers and stir until the solid has dissolved. Titrate with the caustic to pH 8.1 and record the titration.

$$\text{The normality} = \frac{\text{wt of sample taken} \times 1000}{204.1 \times \text{titration, ml}}$$

Barium chloride solution, 10%:	Dissolve 50 gm of C.P. $BaCl_2$ in 500 ml distilled water.
Standard buffer solutions:	pH 4, 7, 10, 12.
Kleenex:	small size (for drying electrodes and stirrers between samples).
Sodium Carbonate, C.P.:	bicarbonate-free. The hydroxide content should be determined so that a correction can be applied for the bicarbonate it consumes when added in Procedure A.

PROCEDURES

First take the pH of the solution as received. If the pH is less than 8.1, use Procedure A (Determination of Sodium Bicarbonate) since hydroxide and carbonate are absent. If the pH is between 8.1 and 11.5, use Procedure A (Determination of Sodium Bicarbonate) and Procedure B (Determination of Carbonate), since hydroxide is absent, and carbonate and bicarbonate are present. If the pH is more than 11.5 use Procedure C (Determination of Carbonate and Hydroxide) since bicarbonate is absent. If the pH is between 11.5 and 3.2, and only a small amount of sample is available, use Procedure D for both carbonate and bicarbonate, but note that the bicarbonate figure then includes carbonate complexed by uranium.

If the pH is less than 3.2, it is unlikely that any of the ionic species considered here are present.

Procedure A:—Determination of Sodium Bicarbonate (initial pH less than 11.5)

Pipette a 50- or 100-ml aliquot of the sample into a 250-ml tall-form beaker. Dilute to 100 ml with water, if necessary. If the Beckman Autotitrator or a pH meter is being used, check the setting of the instrument with pH 10 buffer. Insert the electrodes, set the temperature correcting dial on the instrument to the solution temperature, and titrate to a pH of 11.3, using standard 2.0N sodium hydroxide. Record the titration.

NOTE: If there is a tendency for uranium to precipitate during the titration (as with very concentrated uranium solutions), interrupt the titration and add a gm of bicarbonate-free sodium carbonate. Stir till the precipitate redissolves, then continue the titration. Run a blank on the sodium carbonate used, and correct for any free caustic (which will lower the bicarbonate content).

Calculation

$$\text{gm/l Sodium Bicarbonate} = \frac{\text{Titration (ml)} \times \text{Normality (NaOH)} \times 84}{\text{Aliquot taken ml}}$$

Procedure B:—Determination of Carbonate (Hydroxide Absent) (initial pH between 8.1 and 11.3)

Pipette an aliquot of the sample into a 250-ml beaker (10 ml is suitable for 5% sodium carbonate solutions) and dilute to 100 ml with water. Check the setting of the Autotitrator with pH 7 buffer. Insert the electrodes in the sample solution and set the temperature correcting dial on the instrument to the solution temperature. Titrate to a pH of 8.1 with standard hydrochloric acid (0.2N). Record the number of ml of acid used.

Calculation

$$\text{gm/l Sodium Carbonate} = \frac{\text{Titration (ml)} \times \text{N (HCl)} \times 106}{\text{aliquot taken, ml}}$$

Procedure C:—Determination of Carbonate and Hydroxide (initial pH greater than 11.5)

Pipette duplicate aliquots of the sample (10 ml is suitable for 5% sodium carbonate solution) into 250-ml beakers and dilute to 100 ml with water. Check the setting of the Autotitrator with pH 7.0 buffer.

1. *Determination of Carbonate plus Hydroxide*

Insert the electrodes in the first beaker, set the temperature correction dial to the temperature of the solution, titrate to pH 8.1 with standard 0.2N hydrochloric acid, and record the titration. (T_1).

2. *Determination of Hydroxide*

To the second beaker add 15 ml of 10% barium chloride solution.* Stir and let stand 2 or 3 minutes. Titrate this portion to pH 9.2 with the standard acid and record the titration. (T_2).

Calculation

$$\text{gm/l Sodium Carbonate} = \frac{(T_1 - T_2) \times N\ (HCl) \times 106}{\text{aliquot taken, ml}}$$

$$\text{gm/l Sodium Hydroxide} = \frac{T_2 \times N(HCl) \times 40}{\text{aliquot taken, ml}}$$

Procedure D:—Special Procedure for Carbonate and Bicarbonate for use with Small Samples (carbonate in uranium and thorium complexes included in bicarbonate figure) (initial pH 4.0 to 11.5)

Pipette an aliquot of the sample into a 250-ml beaker (5 ml is suitable for 5% sodium carbonate solutions) and dilute to 100 ml with water. Use either the Precision Dow Recordomatic Titrator (particularly for thorium-bearing solutions) or the Beckman Autotitrator. Check the instrument with pH 7 buffer, wash the electrodes and titrate with N/10 hydrochloric acid. Record the entire curve to pH 3.0 if the recording instrument is used, and note the titration volume to the inflection near pH 8.1, and the titration volume from this inflection to the one near pH 4.2. If thorium is absent use the Autotitrator and titrate to these pH values noting the titration volume to pH 8.1, and that from pH 8.1 to pH 4.2. Record the two titrations, calling the one to pH 8.1, T_1, and the one from pH 8.1 to pH 4.2, T_2. The actual pH of the second end-point in the presence of uranium can be taken from Figure 1.

Calculation

$$\text{gm/l } Na_2CO_3 = \frac{T_1\ (ml) \times N(HCl) \times 106}{\text{aliquot taken, ml}}$$

$$\text{gm/l } NaHCO_3 \text{ (uncorrected for uranium or thorium complexes)} = \frac{(T_2 - 2T_1) \times N(HCl) \times 84}{\text{aliquot taken, ml.}}$$

Report these values as noted here (i.e. it must be made clear that the bicarbonate figure is not corrected for uranium and thorium complexes).

* This amount is sufficient for a 10-ml aliquot of 50 gm/l sodium carbonate if no sulphate is present. In the presence of sulphate, add an additional 1 ml for every 7 gm/l of sodium sulphate present.

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The Gravimetric Determination of Copper by Electrodeposition

METHOD Cu-1

SCOPE

The following method is applicable to all ores, mill products etc. It is the most accurate of all methods for samples containing copper in sufficient amounts to be determined gravimetrically. The volumetric iodide method, although nearly as accurate as the electrolytic method, is more restricted in range. It is, however, less subject to interfering elements. Trace amounts (i.e. microgram quantities) should be determined colorimetrically.

RANGE

The electrolytic method is suitable for the determination of from 0.005 to 5 gm of copper with a precision of about ± 0.1 percent.

OUTLINE

In the following method, copper is electroplated, from a sulphuric-nitric acid solution on a weighed platinum gauze cathode which is then reweighed. For fast routine analysis the solution is stirred and electrolyzed with a current of 1 to 1.5 amperes and 4 volts for 30 to 45 minutes. For more accurate results, the electrolysis should be carried out, in an unstirred solution, for 12 to 18 hours with a current of 0.5 amperes and 2 volts.

The electrolytic deposit should be salmon pink in colour, silky in texture and adherent. Dullness in colour indicates oxidation or the presence of foreign elements. A spongy or coarsely crystalline deposit usually yields high results. Dissolution of the copper in nitric acid and replating often improves the texture and colour and decreases contaminants.

Dissolution of copper ores, minerals and precipitates can usually be accomplished by attack with mineral acids. The ore is first treated with a mixture of hydrochloric and hydrobromic acids to dissolve oxidized materials and to remove some, or most, of the arsenic, antimony and germanium. Nitric acid is then added to dissolve sulphide minerals. Silicates or insoluble material require treatment with hydrofluoric acid, or fusion with potassium pyrosulphate or sodium carbonate, or both. In this case, the nitric acid solution is evaporated to a small volume, taken up with distilled water, and filtered. Most of the copper, lead, silver, etc., will be in the filtrate. The residue, which may contain niobium, tantalum, tungsten, tin, and silica if present, is ignited (in a porcelain crucible if tin, mercury or lead are present) and fused with potassium pyrosulphate. The melt is digested with nitric and hydrochloric acid and filtered. If the easily reducible metals are absent, the residue is treated with hydrofluoric

acid in a platinum crucible to remove silica, fused, digested and filtered. The combined filtrates are fumed nearly to dryness with sulphuric acid, taken up with water plus a few drops of hydrochloric acid and filtered to remove such interfering elements as lead, silver and mercury.

Selenium and tellurium can be removed by acidifying, saturating the filtrate with sulphur dioxide, boiling to expel most of the sulphur dioxide and filtering, but this step is not included in the method. The copper is separated from iron, cobalt, nickel, etc., by precipitating it from a 5-6 percent hydrochloric acid solution, with hydrogen sulphide. Arsenic, antimony, selenium, tellurium, molybdenum, tin, gold, etc. ,are then eliminated by precipating the copper with hydrogen sulphide from an alkaline solution. Finally bismuth is removed by precipitating it with an excess of ammonium hydroxide. Rhodium, palladium and osmium, which also interfere, are seldom encountered.

Copper can also be separated from solutions containing iron, nickel, cobalt, zinc, cadmium, arsenic, antimony, manganese, bismuth and tin by precipitating the copper as insoluble cuprous thiocyanate, after reduction with sulphurous acid, in a feebly acid solution. Precipitation can be carried out in the presence of 1 percent by volume of either hydrochloric or sulphuric acids, preferably the former if much arsenic is present. Addition of 1-2 gm of tartaric acid prevents the hydrolysis of bismuth, antimony and tin. The solution should not contain more than about 0.2 gm of copper per 100 ml and a three- to five-fold excess of precipitant should be used. The precipitate is somewhat soluble in strong concentrations of the precipitant, so that a larger excess is undesirable. In routine analysis the precipitate may be filtered hot, but in more accurate analysis the solution should be allowed to cool before filtering. Oxidizing agents, high acidities and excessive amounts of ammonium salts or of thiocyanate interfere in the precipitation. Lead, mercury, selenium, tellurium and the precious metals will contaminate the precipitate. Of these, lead will not interfere in the electrolytic method for copper and lead, silver or mercury do not interfere in the volumetric iodide method. Thioacetamide can be used instead of hydrogen sulphide in the hydrogen sulphide separations.

APPARATUS

Beakers, Griffin:	250 and 400 ml sizes.
Filter paper:	Whatman No. 30 and No. 42.
Crucibles, porcelain:	Coors size 1A.
Crucibles, platinum:	25 ml.
Hot plate:	
Meker burner:	
Tripod:	
Triangles, silica covered:	
Electroplating apparatus with magnetic stirrer (*see* Figures 1A and 1B):	Custom model (4)
Funnels, 65 mm, long stem:	
Pipettes, volumetric, 5, 10, 25, 50 ml:	

Burette:	50 ml.
Six volt battery:	
Battery charger:	
Ovens:	
Desiccator:	
Platinum cathode (gauze):	at least two.
Platinum anode (spiral):	at least two.
Crucible tongs, platinum tipped:	
Crucible tongs, stainless steel:	
Beaker tongs:	
Wash bottles:	1000 ml.
Electrolytic beakers:	Berzelius 100, 200, and 300 ml sizes.
Steam bath:	

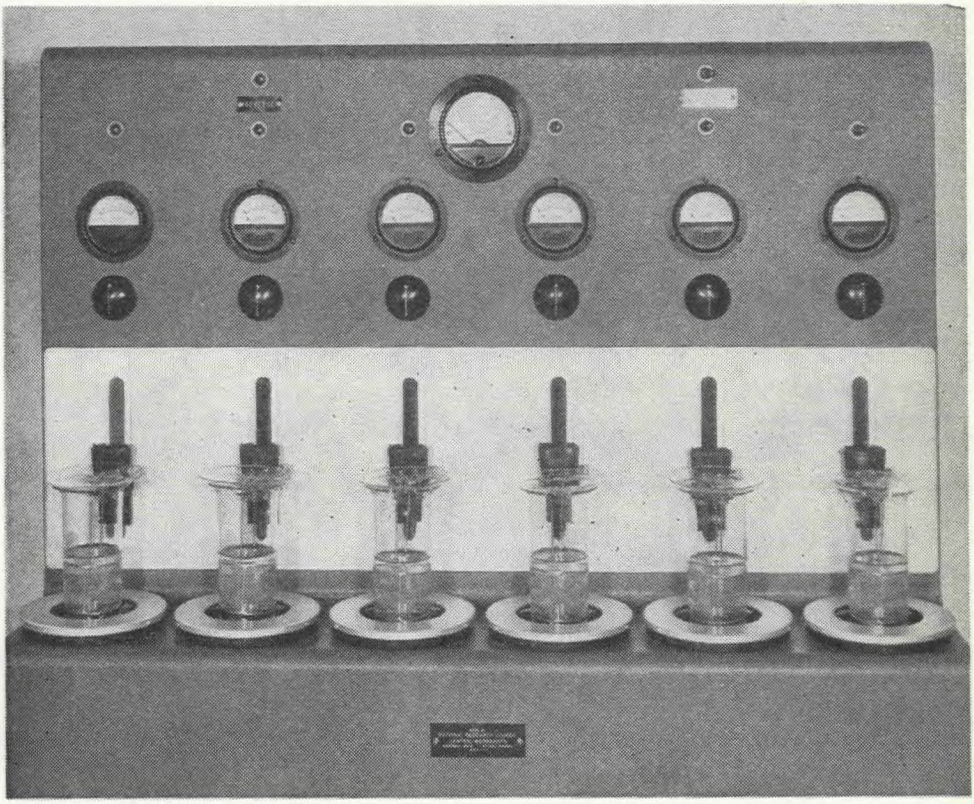

FIG. 1A—ELECTRODEPOSITION APPARATUS (MINES BRANCH MODEL). (4) FRONT VIEW.

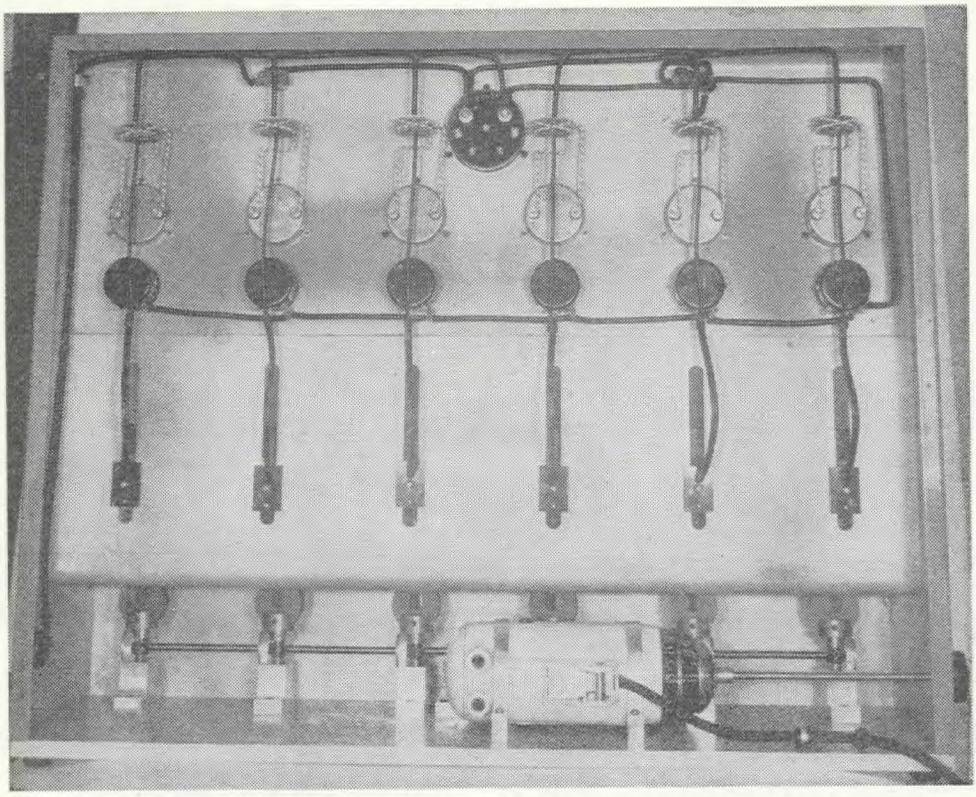

FIG. 1B—ELECTRODEPOSITION APPARATUS (MINES BRANCH MODEL). REAR VIEW.

REAGENTS

Sodium carbonate:

Potassium nitrate:

Potassium pyrosulphate:

Hydrochloric acid:

Hydrobromic acid:

Nitric acid:

Sulphuric acid:

Sulphuric acid, dil: 1:1 v/v.

Bromine:

Bromine water: a saturated solution of bromine in distilled water.

Hydrogen sulphide: cylinder or lecture bottle.

Thioacetamide:

Thioacetamide solution: 1 percent aqueous solution.

Sodium sulphite:

Sodium hydroxide:

Sodium sulphide wash solution: Dissolve 30 gm of sodium hydroxide in 1 litre of water and saturate with hydrogen sulphide. Add 3 gm of sodium hydroxide and store in a wash bottle.

Ammonium hydroxide:

Ammonium hydroxide wash solution: 10 ml of ammonium hydroxide diluted to 1 litre.

Potassium thiocyanate:

Tartaric acid:

Potassium thiocyanate—sodium sulphite solution: An aqueous solution containing 2 percent potassium thiocyanate and 2 percent sodium sulphite.

Ammonium sulphate:

Ammonium sulphate wash solution: An aqueous solution containing 1 percent ammonium sulphate.

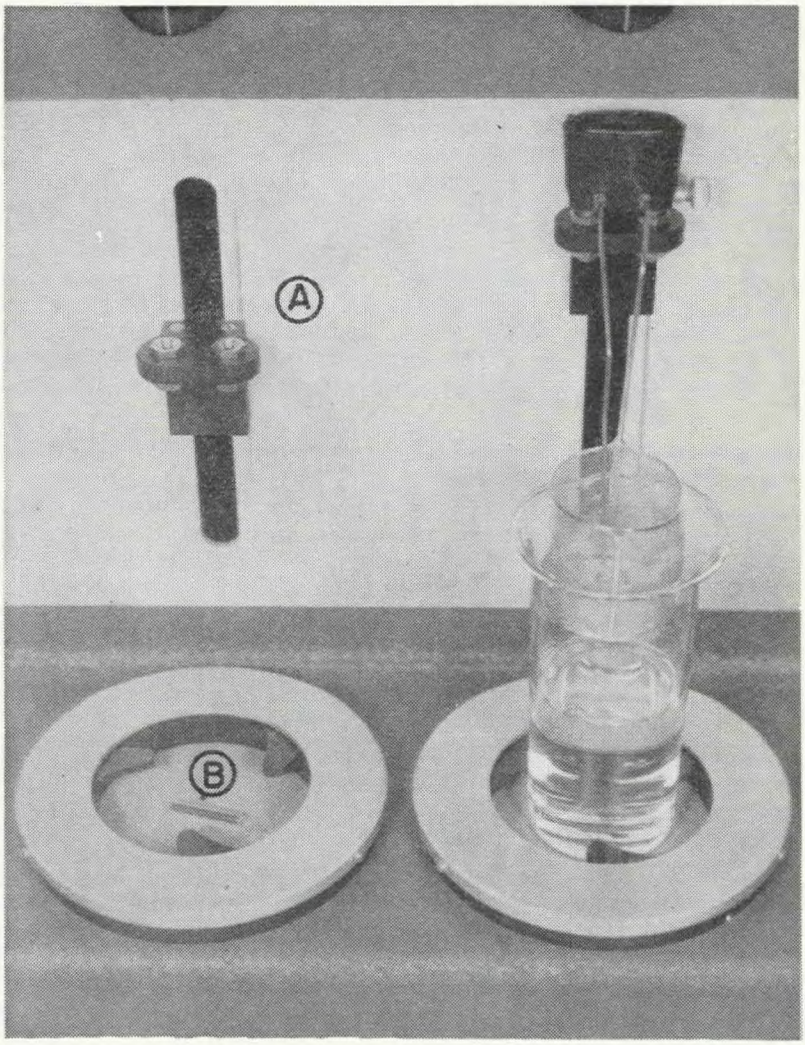

FIG. 2—ELECTRODEPOSITION APPARATUS. (CLOSE-UP SHOWING CONTACTS "A" AND MAGNETIC STIRRER "B").

PROCEDURE

A. Decomposition and Preliminary Treatment

1. *Ores, Precipitates and Alloys*

Weigh out a portion of the sample, preferably containing 0.02 to 0.2 gm of copper, into a 250-ml beaker. Add 25 ml of dilute hydrochloric acid (1:1, v/v) and 10 ml of hydrobromic acid. Heat to boiling and boil for 15 minutes. Cool and cautiously add 10 ml of nitric acid, 10 ml of dilute sulphuric acid (1:1, v/v) and evaporate to heavy fumes. If the arsenide or sulphide content is high, repeat the hydrochloric-hydrobromic and the nitric acid treatments and again evaporate to heavy fumes. Cool slightly, wash down the sides of the beaker, and evaporate just to dryness, but do not bake.

(a) *Easily Reducible Metals Present*—If lead, silver, mercury or other easily-reducible metals are present, digest the evaporated residue in 20 ml of water containing 2 ml of nitric acid until the soluble salts are in solution. Filter through a Whatman No. 30 filter paper and wash the paper with hot water. Reserve the filtrate and examine the material on the filter.

If the amount of insoluble residue is small and it is light in colour, discard it. Add 6 ml of dilute sulphuric acid (1:1, v/v) to the filtrate and evaporate to copious fumes. Cool, wash down the sides of the beaker with distilled water and evaporate just to dryness. Digest with 20 ml of water containing 2 ml of hydrochloric acid until the soluble salts are in solution. Filter through a Whatman No. 30 filter paper into a clean beaker, wash the paper and residue with hot water and discard the residue. Proceed with the required separations as outlined in the following sections.

If the amount of insoluble residue is large, or if it is highly coloured, transfer the paper and residue to a porcelain crucible, dry, char, and burn off the filter paper. Fuse the residue with 3 gm of potassium pyrosulphate. Transfer the cooled crucible and melt to the original beaker, and digest the melt in 20 ml of water until it disintegrates. Add 2 ml of nitric acid and 5 ml of dilute sulphuric acid (1:1, v/v), and evaporate to heavy fumes. Cool, wash down the sides of the beaker with distilled water and evaporate just to dryness. Digest with 20 ml of water containing 2 ml of hydrochloric acid until the soluble salts are in solution. Filter through a Whatman No. 30 filter paper into a clean beaker, and wash the paper and residue with hot water. Proceed with the required separations as outlined in the following sections.

(b) *Easily Reducible Metals Absent*—If lead, silver, mercury etc. are absent, digest the evaporated residue with 20 ml of water containing 2 ml of hydrochloric acid. Filter through a Whatman No. 30 filter paper and wash the paper with hot water. Reserve the filtrate and examine the material on the filter.

If the amount of insoluble residue is small and it is light in colour, discard it and proceed with those separations described below which are required on the basis of the interfering elements present.

If the amount of the insoluble residue is large or the residue is highly coloured, transfer the paper and residue to a 30-ml platinum crucible. Dry, char and burn off the filter paper. Add 10 ml of hydrofluoric acid and 2 ml of dilute sulphuric acid (1:1, v/v). Heat to volatilize the silica and then fuse the residue with either 3 gm of potassium pyrosulphate, or 3 gm of potassium carbonate plus a little potassium nitrate. Transfer the cooled crucible and melt to the original beaker and digest it in 20 ml of water until it disintegrates. Add 2 ml of nitric acid, 5 ml of dilute sulphuric acid (1:1, v/v) and evaporate to heavy fumes. Do not bake. Digest with 20 ml of water containing 2 ml of

hydrochloric acid until the soluble salts are in solution. Filter through a Whatman No. 30 filter paper into a clean beaker and wash the paper and residue with hot water. Discard the residue. If proceeding to the "Hydrogen Sulphide Separation" (Section B), no further treatment is necessary.

If proceeding directly to the "Cuprous Thiocyanate Separation" (Section D), (i.e. omitting the Hydrogen Sulphide Separation), neutralize the solution with 5% sodium hydroxide solution until a permanent precipitate begins to form, clear with a few drops of hydrochloric acid and add 1 ml in excess. Dilute to 100 ml and continue with the Cuprous Thiocyanate Separation.

2. *Solutions*

Transfer a suitable aliquot to a beaker, add 4 ml nitric acid, 6 ml dilute sulphuric acid (1:1, v/v) and evaporate to heavy fumes. Cool, wash down the sides of the beaker with a little water, and evaporate just to dryness. Repeat the nitric-sulphuric acids treatment if large amounts of organic material are present. Dissolve the residue in 20 ml of water containing 2 ml of hydrochloric acid. Filter, if necessary, into a clean beaker, and carry out the separations required, by the procedures outlined in the following sections.

B. Hydrogen Sulphide Separation

Dilute the filtrate or combined filtrates from one of the above methods of digestion to about 100 ml, add 1 gm of sodium sulphite and boil until all the excess sulphur dioxide is expelled. Add 3 ml of hydrochloric acid, heat to boiling and bubble hydrogen sulphide through the solution for 15 minutes. Dilute to 150 ml with distilled water and continue bubbling hydrogen sulphide through the solution for 10 minutes. Filter through a Whatman No. 42 filter paper and wash the precipitate with cold acidulated hydrogen sulphide water (1% hydrochloric acid solution v/v, saturated with hydrogen sulphide). Do not let the filter paper become dry or drained during filtration or washing. Discard the filtrate and washings unless such elements as iron, nickel, cobalt, uranium, aluminum etc., are to be determined on the same portion of the sample.

If the precipitate is large, or if the above elements are being determined, wash most of the precipitate back into the beaker, place the beaker under the funnel and dissolve the remaining precipitate from the paper, first with a warm nitric acid-bromine solution (10 ml of nitric acid added to 10 ml of bromine water), and then with a little hot water. Add 5 ml of 1:1 sulphuric acid and evaporate to heavy fumes of sulphur trioxide. Cool, wash down the sides of the beaker with water and evaporate just to dryness. Digest the residue with 5 ml of hydrochloric acid and 30 ml of water, until the soluble salts are in solution. Dilute to 100 ml, bubble hydrogen sulphide through the solution for 30 minutes, filter and wash as before. Combine the filtrates with the reserve filtrate above, if it is to be used for further analyses.

If the precipitate is small, or if a second hydrogen sulphide precipitation has been performed, and the amount of arsenic, selenium, antimony, tin, molybdenum and tellurium is slight, wash the paper and precipitate thoroughly with a sodium sulphide-sodium hydroxide wash solution (a 3% aqueous solution of sodium hydroxide saturated with hydrogen sulphide plus an additional 3 gm of sodium hydroxide). Discard the filtrate and washings.

If the precipitate is large, and/or the above elements are present in considerable quantities, transfer most of the precipitate into the beaker. Dilute to 100-150 ml with distilled water, add 3 gm of sodium hydroxide and digest on the hot plate. Bubble hydrogen sulphide through the solution for 15 minutes. Add 2 gm more of sodium hydroxide, filter through the same filter paper and wash the paper and precipitate with the sodium sulphide-sodium hydroxide wash solution. Discard the filtrate and washings.

Regardless of which of the foregoing procedures has been used, wash most of the precipitate back into the beaker, place the beaker under the funnel and dissolve the precipitate from the paper, first with a warm nitric acid-bromine solution (10 ml of nitric acid added to 10 ml of bromine water), and then with a little hot water. Add 5 ml of 1 :1 sulphuric acid to the solution and evaporate to 3 ml.

If no other separations are required, dilute the sulphuric acid solution, transfer to an electrolytic beaker and make to 100 ml. Add 1 ml of nitric acid and proceed with the "Electrodeposition Step" (Section E).

If the Cuprous Thiocyanate Separation is required, continue evaporating the sulphuric acid solution to dryness. Do not bake. Cool and wash down the sides of the beaker with a little water. Add an additional 2-3 ml of sulphuric acid and again evaporate just to dryness. Add 20-30 ml of water, 1 ml of hydrochloric acid and digest until the soluble salts are in solution. Dilute to 100 ml, filter if necessary and proceed with the Cuprous Thiocyanate Separation.

C. Ammonium Hydroxide Separation

If bismuth is present, dilute to 150 ml with distilled water, heat to boiling and add an excess of ammonium hydroxide. Digest on the hot plate for 15 minutes and filter through a No. 30 Whatman filter paper into a clean beaker. Wash the paper and precipitate with a warm 1% ammonium hydroxide solution. Discard the precipitate. Evaporate the filtrate to a small volume, add nitric acid and continue the evaporation until most of the ammonium salts are driven off. Add additional nitric acid, if required, and evaporate to dryness. Dissolve the copper in 50 ml of water, 1.5 ml of nitric and 5 ml of 1:1 sulphuric acid. Transfer to an electrolytic beaker, cool, dilute to 100 ml and electroplate the copper as outlined in Section E.

D. Cuprous Thiocyanate Separation

To the solution from any of the foregoing sections which has been prepared for this separation, add 2-3 gm of tartaric acid and then add a 10% aqueous solution of sodium sulphite in 20-ml portions until, after standing on a steam bath for 30 minutes, the solution still smells of sulphur dioxide and is a pale yellow. Adjust the acidity to 1%, by volume, with hydrochloric acid and then with constant stirring add dropwise, from a burette, a 2% solution of potassium thiocyanate containing 2% sodium sulphite, until precipitation ceases, plus a threefold excess. Cool, let stand for 4 hours or preferably overnight, and filter through a No. 42 Whatman paper. Wash the paper and precipitate with a cool 1% solution of ammonium sulphate. Discard the filtrate. Transfer the paper and precipitate to a porcelain crucible, dry, char, and burn off the filter paper. Dissolve the residue in 2 ml of nitric acid and 10 ml of water. Transfer to an electrolytic beaker, dilute to 150 ml, add 5 ml of 1:1 sulphuric and electroplate the copper as outlined in the following.

E. Electrodeposition Step

Weigh a clean dry platinum gauze cathode. Insert the cathode in the beaker so that its surface clears the platinum anode by at least 5 mm. Lower the electrodes into the electrolyte, turn on the stirring mechanism and electroplate for 30 minutes at 1 ampere and 4 volts. For a more accurate analysis the beaker should be covered with a split watch glass and electro-plated from an unstirred solution for 12 to 18 hours with a current of 0.5 ampere and 2 volts. Rinse down the sides of the beaker, immerse the electrodes a little farther into the solution and continue the electrolysis to ensure that all the copper is removed from the solution. Gradually raise the electrodes from the solution, with the current still turned on, and wash thoroughly with distilled water. Rinse the cathode in ethyl alcohol, dry for 3 minutes at 100°C, cool in a desiccator, and weigh. If the deposit is off-colour or appears spongy or crystalline, dissolve the deposit in 100 ml of water and 2 ml of nitric acid. Add 3 ml of 1:1 sulphuric acid, replate, and weigh as before.

CALCULATIONS

Solids

$$\% \text{ Cu} = \frac{\text{wt. deposit} \times 100}{\text{wt. sample, gm}}$$

Solutions

$$\text{gm/l Cu} = \frac{\text{wt. deposit} \times 1000}{\text{sample vol. taken, ml.}}$$

If no weighable deposit is obtained, the results should be reported as "less than" the minimum amount detectable, rather than using the term "not detectable". Assuming the minimum weighable amount is 0.0005 gm then any amount less than 0.0005 gm should be reported as

$$\text{less than } \frac{0.0005 \times 100}{\text{wt. of sample}} \% \text{ for solids}$$

$$\text{and less than } \frac{0.0005 \times 1000}{\text{sample vol.}} \text{ gm/l for solutions.}$$

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The Colorimetric Determination of Copper with Cuproine

METHOD Cu-2

SCOPE

This method is applicable to all types of samples. It is preferred for use with large numbers of samples, and for trace amounts. For the occasional determination of copper, the electrolytic method may be found more convenient.

RANGE

The method will determine copper down to 0.001%, based on use of a 1-gm sample and 1-cm spectrophotometer cells.

OUTLINE

Cuproine (2, 2'-biquinoline) forms a purple complex with cuprous copper, with the composition $(Cu(cuproine)_2)^+$. The colour, which can be developed in alcoholic or acetic acid medium, (1) or in amyl alcohol (2), absorbs light strongly at a wave length of 545 mμ.

Copper, normally present in the cupric form, is reduced to the cuprous state with hydroxylamine hydrochloride. Tartaric acid is added to complex iron, aluminum and other ions which would give hydrolytic precipitates at the pH used for extraction.

Extraction of the complex by amyl alcohol is quantitative over the pH range 4.5 to 7.5 and is carried out at pH 5.0 to 6.0. (3) The only known interference is mercury, which forms a precipitate (4).

APPARATUS

Beakers, Pyrex, Griffin low form:	250 ml and 100 ml sizes.
Funnels, filtering, Bunsen long stem:	
Crucibles, porcelain:	Coors No. 1a.
Pipettes, volumetric:	
Flasks, volumetric:	
Funnels, separatory, Squibb pear shaped:	60 ml size, stopcocks and stoppers lubricated with silicone grease.
Funnel racks:	
pH meter:	
Spectrophotometer:	
Spectrophotometer cells, Corex:	1 cm and 5 cm sizes.
Centrifuge, Safety type:	with head to accommodate 15 ml test tubes.
Centrifuge tubes:	15 ml size.

REAGENTS

Nitric acid, concentrated:	
Hydrochloric acid, concentrated:	
Hydrochloric acid, dil:	1:1 v/v.
Hydrochloric acid wash solution:	1:100 v/v.
Sulphuric acid, dil:	1:1 v/v.
Sodium peroxide:	
Hydroxylamine hydrochloride, 10% solution:	w/v.
Tartaric acid, 10% solution:	w/v.
Ammonium hydroxide, dil:	1:1 v/v.
Cuproine solution, 0.02%:	0.02 gm 2, 2′ biquinoline in 100 ml of amyl alcohol.
Amyl alcohol:	
Filter paper, Whatman No. 40:	7 cm size.
Silicone grease:	
Standard copper solution:	Dissolve 0.502 gm $CuSO_4$ in water, transfer to a 100 ml volumetric flask and dilute to volume. Pipette 1.0 ml of this solution into a second 100 ml volumetric flask and again dilute to volume. 1 ml of this solution = 20 γ Cu.

Preparation of the Calibration Graph

Pipette aliquots of the standard copper solution, covering the range 10 to 80γ Cu, into 100-ml beakers. Carry through a blank as well. Adjust the volumes to about 10 ml with water. Add 5 ml of hydroxylamine hydrochloride solution (w/v) and 5 ml of tartaric acid solution. Using a pH meter standardized at pH 4.0, adjust the pH to 5.0-6.0 with dilute ammonium hydroxide. Rinse off the electrodes into the beaker and transfer the solutions to a 60-ml separatory funnel (stopcock and stopper greased with silicone grease). Keep the volume of solution plus washings at 40 ml.

Add by pipette 10 ml of cuproine-amyl alcohol solution. Shake the mixture for 1 to 2 minutes. Discard the aqueous layer and draw off the organic layer into a 15-ml centrifuge tube. Centrifuge it for 1 minute to clear up any cloudiness. Read the standards against the blank in 1-cm cells at a wave length of 545 mμ. Plot a curve of copper (γ per 10 ml) as abscissa against optical density as ordinate.

PROCEDURE

A. Decomposition and Preliminary Treatment

1. *Solid Samples*

Weigh accurately 1 gm of sample into a 250-ml beaker. Add 20 ml dil. hydrochloric acid and boil for 10 minutes. Cool, add 5 ml concentrated nitric acid, 10 ml dil. sulphuric acid and evaporate the sample to dryness on the hot plate. Dissolve the soluble salts in 5 ml of concentrated hydrochloric acid and 50 ml water. Bring the sample to a boil, cover and digest 15 minutes just below boiling. Filter off the insoluble residue on a Whatman No. 40 paper and wash

the residue with hydrochloric acid wash solution. Reserve the filtrate. If the residue is suspected to contain copper, transfer it to a porcelain crucible, dry and ignite it. Mix with 5 to 15 times its weight of sodium peroxide and sinter 30 minutes at 400°C (or 7 minutes at 480°C). Cool and transfer the crucible to a 250-ml beaker. Add 25 ml water, digest the melt and cautiously acidify with hydrochloric acid. Add the solution to the main volume of filtrate. Transfer the combined filtrates to a volumetric flask and dilute to volume. Choose a flask such that a 10-ml aliquot will contain about 50γ of copper.

2. *Solutions*

Pipette a suitable aliquot into a volumetric flask, choosing the dilution to provide 50γ Cu in the final 10-ml aliquot taken for extraction. Neutralize to about pH 4, if basic, and add 3 to 5 drops of hydrochloric acid in excess. Dilute to volume.

B. Colour Development

Pipette a 10-ml aliquot into a 100-ml beaker. Add 5 ml of 10% hydroxylamine hydrochloride solution and 5 ml of 10% tartaric acid solution. At the same time, add the same reagents to an empty beaker to serve as a blank. By means of a pH meter standardized at pH 4, adjust the pH of the solution to 5.0 to 6.0 with dil. ammonium hydroxide. Rinse off the electrodes into the beaker and transfer the solution quantitatively to a 60-ml separatory funnel, (stopcock and stoppers lubricated with silicone grease), keeping the volume of sample plus washings at 40 ml.

Add by pipette 10 ml of cuproine: amyl alcohol solution. Shake the mixture for 1 or 2 minutes. Discard the aqueous layer and draw off the organic layer into a 15-ml centrifuge tube. Centrifuge 1 minute to clear up any cloudiness in the organic extract. Read the sample against the reagent blank in the spectrophotometer at 545 mμ using 1-cm cells. Record the optical density and read the corresponding copper content from the calibration graph.

CALCULATIONS

$$\% \text{ Cu} = \frac{\gamma \text{ Cu/10 ml (from graph)}}{10^9} \times \frac{\text{final dil'n, ml}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt. gm.}}$$

$$\text{gm/l Cu} = \frac{\gamma \text{ Cu/10 ml (from graph)}}{10^9} \times \frac{\text{final dil'n, ml}}{\text{aliquot taken}} \times \frac{1000}{\text{sample vol. ml}}$$

If no colour is obtained, the result should be reported as "less than" the limit of detection. This corresponds to 5γ Cu for the procedure as described and the figure to report may be calculated on this basis

$$\% \text{ Cu} = \frac{5}{10^9} \times \frac{\text{final dil'n, ml}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

References

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The Volumetric Iodide Method for the Determination of Copper

METHOD Cu-3

SCOPE

The following method is applicable to all ores and mill products. It is nearly as accurate as the electrolytic method and is less subject to interference by elements such as zinc, pentavalent arsenic and antimony, lead, bismuth and silver. It is, however, more restricted in range than the electrolytic method.

RANGE

The volumetric iodide method is suitable for the determination of from 0.005 to 0.25 gm of copper with a precision of about 1 percent.

OUTLINE

The method is based upon the fact that cuprous iodide and iodine are formed when an acidified solution of cupric salts is treated with potassium iodide. The liberated iodine is titrated with a standard thiosulphate solution using a starch indicator solution. Addition of ammonium thiocyanate sharpens the end-point (5).

$$2\ CuSO_4 + 4\ KI \longrightarrow Cu_2I_2 + 2\ K_2SO_4 + I_2$$

$$2\ Cu\ (C_2H_3O_2)_2 + 4\ KI \longrightarrow Cu_2I_2 + 4\ KC_2H_3O_2 + I_2$$

$$2\ Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2\ NaI$$

Interfering elements such as iron are eliminated by precipitating the copper with hydrogen sulphide. Selenium and tellurium can be removed by precipitating them from a hydrochloric acid solution with sulphur dioxide but this step is not included. Trivalent arsenic and antimony are either converted to the pentavalent state with nitric acid and bromine water or are removed by precipitating the copper as cuprous thiocyanate. The latter method also eliminates iron and elements such as bismuth which consume iodide (1-5).

APPARATUS

Beakers, Griffin:	250 and 400 ml sizes.
Filter paper:	Whatman Nos. 30 and 42.
Crucibles, porcelain:	Coors size 1A.
Crucibles, platinum:	25 ml size.
Hot plate:	
Meker burner:	
Tripod:	
Triangles:	silica covered.

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Cu-3

Funnels:	
Pipettes, volumetric:	5, 10, 25, 50 ml
Burettes:	50 ml.
Beaker tongs:	
Crucible tongs:	stainless.
Crucible tongs:	platinum tipped.
Wash bottles:	1000 ml.
Steam bath:	

REAGENTS

Acetic acid, glacial:	
Sodium carbonate:	
Potassium pyrosulphate:	
Hydrochloric acid:	
Hydrobromic acid:	
Nitric acid:	
Sulphuric acid:	
Bromine:	
Bromine water:	a saturated solution of bromine in water.
Sulphuric acid:	1:1. v/v.
Hydrogen sulphide:	cylinder or lecture bottle.
Sodium sulphite:	
Sodium hydroxide:	
Sodium sulphide wash solution:	Dissolve 30 gm of sodium hydroxide in 1 litre of water and saturate with hydrogen sulphide. Add 3 gm of sodium hydroxide and store in a wash bottle.
Potassium thiocyanate-tartaric acid solution:	An aqueous solution, 1% in potassium thiocyanate and 1% in tartaric acid.
Potassium thiocyanate-sodium sulphite solution:	An aqueous solution containing 2 percent potassium thiocyanate and 2 percent sodium sulphite.
Ammonium sulphate:	
Ammonium sulphate wash solution:	An aqueous solution containing 1 percent ammonium sulphate.
Potassium iodide:	
Sodium thiosulphate:	
Borax:	
Soluble starch:	
Starch solution:	Triturate 2 gm of soluble starch in a little cold water to a thin paste. Slowly add 200 ml of boiling water and boil until an almost clear liquid is obtained. Cool, add 2 gm of potassium iodide, let stand overnight and filter into a reagent bottle.
Copper foil or wire:	(electrolytic).
Sodium thiosulphate, standard solution, strong:	Dissolve 19.522 gm of $Na_2S_2O_3 . 5 H_2O$ in 1 litre of freshly boiled and cooled distilled water, add 3 gm of borax and standardize against pure copper foil or wire (see below). 1 ml ≑ 0.005 gm Cu.
Sodium thiosulphate standard solution, weak:	Dilute 200 ml of the strong standard to 500 ml. 1 ml ≑ 0.002 gm of copper.
Potassium nitrate:	

Standardization of Sodium Thiosulphate Solution

Weigh 0.1000 gm of pure copper foil or wire into a 200-ml Erlenmeyer flask. Add 20-30 ml of water and 2-3 ml of nitric acid. Boil to remove oxides of nitrogen. Add 5 ml of bromine water and boil until the excess bromine is expelled. This step assures removal of the last of nitrous oxides. Cool, add ammonium hydroxide until the solution just turns blue and a slight excess of ammonia is present. Boil gently until the odour of ammonium hydroxide is very faint, but still present, then add 5-7 ml of strong acetic acid to dissolve any copper oxide which may have deposited, and cool to room temperature. Add 3 gm of potassium iodide, and titrate the brown solution with sodium thiosulphate until nearly colourless, then add 2-3 ml of starch solution and titrate to the disappearance of the blue colour. The cuprous iodine solution is usually coloured a little by adsorbed iodo-starch and is not pure white at the end-point. The reaction is reversible and the solution may be back titrated with a standard iodine solution. Calculate the factor "f" in gm Cu per ml. If T ml of thiosulphate were used to titrate X gm of copper then:

$$1 \text{ ml of thiosulphate} = \frac{X}{T} = \text{"f" gm Cu}$$

The titre of the thiosulphate solution changes upon standing. Therefore it should be restandardized occasionally.

PROCEDURE

A. Preliminary Treatment

1. *Ores, Initial Acid Attack*

(*a*) *Ores and Precipitates; Silica, Arsenic or Sulphur High*—Weigh a sample, preferably containing 0.05 to 0.2 gm of copper into a 250-ml beaker. Add 20-25 ml of 1:1 hydrochloric acid and 5-10 ml of hydrobromic acid. Heat to boiling and boil for 15-20 minutes. Cool and cautiously add 5-10 ml of nitric acid, 10 ml of 1:1 sulphuric acid, and evaporate to heavy fumes of sulphur trioxide. Repeat the hydrochloric-hydrobromic and the nitric acid treatments and again evaporate to dense fumes of sulphur trioxide. Cool, wash down the sides of the beaker and evaporate just to dryness. If silica is to be determined on the same portion of the sample, bake the residue for 1 hour at 110°C. Take up in 20-30 ml of water and 2-3 ml of nitric acid and digest until the soluble salts are in solution. Filter through a No. 30 Whatman paper into a clean beaker and wash the paper and residue with hot water. Reserve the filtrate and washings.

If the amount of residue is large, if it is discoloured, or if silica is being determined, continue with subsection 2. "Treatment of Insoluble Residues".

If the amount of residue is small and it is light in colour, discard it. Add 5-6 ml of dil sulphuric acid to the filtrate and evaporate it to dense fumes.

Cool, wash down the sides of the beaker and evaporate to dryness. Take up in 20-30 ml of water, 2-3 ml of hydrochloric acid and warm to dissolve the soluble salts. Filter through a No. 30 Whatman filter paper into a clean 250-ml beaker and wash the paper and residue with hot water. Discard this residue. Treat the filtrate as described in Section B, "Separations".

(*b*) *Ores and Precipitates; Silica Low and Easily Reducible Metals Absent*—Weigh a suitable sample (0.05-0.2 gm) Cu into a 250-ml beaker. Add 20-25 ml

of 1:1 hydrochloric acid and 5-10 ml of hydrobromic acid. Heat to boiling and boil for 15-20 minutes. Cool and cautiously add 5 to 10 ml of nitric acid and 10 ml of 1:1 sulphuric acid. Evaporate to heavy fumes, but do not bake.

Add 20-30 ml of water, 2-3 ml of hydrochloric acid, and digest to dissolve the soluble salts. Filter through a No. 30 Whatman filter paper into a clean 250-ml beaker and wash the residue with hot water. Reserve the filtrate and washings.

If the residue is large or discoloured proceed to subsection 2. "Treatment of Insoluble Residues".

If the residue is small and light in colour discard it and proceed to Section B, "Separations".

2. *Treatment of Insoluble Residues From Subsections 1 (a) and 1 (b)*

(*a*) *Easily Reducible Metals Present*—Transfer the residue and paper to a porcelain crucible, dry, char and burn off the paper.

Fuse the residue with 2-3 gm of potassium pyrosulphate. Transfer the cooled melt to the original beaker, add 10-20 ml of water and digest on the hot plate until the mass disintegrates. Add 2-3 ml of hydrochloric acid, 2-3 ml of nitric and 3-5 ml of 1:1 sulphuric acid. Evaporate to heavy fumes. Cool, wash down the sides of the beaker with distilled water and evaporate just to dryness. Digest with 20-30 ml of water and 1-2 ml of hydrochloric acid until the soluble salts are in solution. Filter through a No. 30 Whatman filter paper into the beaker containing the reserve filtrate. Wash the paper and residue with hot water. Discard the residue.

Treat the combined filtrates as described in Section B, "Separations".

(*b*) *Silica Content High, Easily Reducible Metals Absent*—Transfer the residue and paper to a platinum crucible. Dry, char and burn off the filter paper. Add 5-10 ml of hydrofluoric acid and 1-2 ml of dil sulphuric acid to the crucible and heat to volatilize the silica. Evaporate to dryness and add 2-3 gm of potassium pyrosulphate, or 2-3 gm of sodium carbonate plus a little potassium nitrate. Heat over a burner until a quiet fusion is obtained. Cool and transfer the melt to a 250-ml beaker. Add 10-20 ml of water and digest on the hot plate until the mass disintegrates. Add 2-3 ml of concentrated nitric and 3-5 ml of dil sulphuric acid. Evaporate to heavy fumes. Cool, wash down the sides of the beaker with distilled water and evaporate just to dryness. Take up with 20-30 ml of water and 1-2 ml of hydrochloric acid. Digest until the soluble salts are in solution. Filter through a No. 30 Whatman filter paper into the beaker containing the reserve filtrate, washing the paper and the residue with hot water. Discard the residue.

To the combined filtrates, add 5-6 ml of dil sulphuric acid and evaporate to dense fumes. Cool, wash down the sides of the beaker and evaporate to dryness. Take up in 20-30 ml of water and 2-3 ml of hydrochloric acid and digest until the soluble salts are dissolved. Filter through a No. 30 Whatman filter paper into a clean beaker and wash the paper and residue with hot water. Discard this residue also.

Treat the filtrate as described in Section B, "Separations".

3. *Solutions*

Pipette an aliquot of the solution into a 250-ml beaker. Add 3-4 ml of nitric acid and 5-6 ml of 1:1 sulphuric acid. Evaporate to heavy fumes of sulphur trioxide. Cool, wash down the sides of the beaker with distilled water

and evaporate just to dryness. Repeat the nitric-sulphuric acid treatment if large amounts of organic material are present. Dissolve the residue in 20-30 ml of water and 2-3 ml of hydrochloric acid. Filter if necessary into a clean beaker.

Treat the filtrate as described in Section B, "Separations".

B. Separations

1. *Hydrogen Sulphide Separation; Fe, Ni, Co, U, Al Present (omit if these elements are absent)*

Dilute the filtrate or combined filtrates from one of the above methods of treatment to about 100 ml, add 1 gm of sodium sulphite and boil until the excess sulphur dioxide is expelled. Add 2-3 ml of hydrochloric acid, continue heating for a few minutes and filter, if necessary, into a clean beaker. Wash the paper and residue with a warm 1 percent hydrochloric acid solution. Discard the residue. Bubble hydrogen sulphide through the solution, dilute to 150 ml, heat to boiling and continue bubbling hydrogen sulphide through the solution for 5-10 minutes while the solution cools. Filter through a No. 42 Whatman paper and wash the paper and precipitate with cold acidulated hydrogen sulphide water (1 percent hydrochloric acid solution v/v saturated with hydrogen sulphide). Do not let the filter paper or precipitate become dry during filtration or washing. Discard the filtrate and washings unless such elements as iron, nickel, cobalt, uranium and aluminum are being determined on the same portion of the sample. Wash most of the precipitate back into the beaker with a little distilled water. Add 6-7 ml of nitric acid and boil to expel oxides of nitrogen. Pour the solution through the filter paper to dissolve any remaining sulphides and wash the paper first with a little bromine water and then wash the beaker and paper with a little hot water. Boil the filtrate until the excess bromine is expelled.

2. *Second Hydrogen Sulphide Separation; Samples High in Fe, Ni, Co, U and Al (omit if these elements low or not being determined in the filtrate)*

To the solution from Section B.1, add 4-5 ml of 1:1 sulphuric acid and evaporate to dryness. Dissolve the residue with water and hydrochloric acid and reprecipitate the copper with hydrogen sulphide as outlined in Section B.1.

3. *Cuprous Thiocyanate Separation; Samples High in As, Sb and Bi (omit if these elements low or not being determined in the filtrate)*

To the solutions from Section A, 1, 2 or 3, or from Section B, 1 or 2, add 1 gm of sodium sulphite and heat to boiling. Filter, if necessary, into a clean beaker and wash the precipitate and paper with hot water. Discard the residue. Neutralize the filtrate with a 5 percent solution of sodium hydroxide until a permanent precipitate forms. Clear with a few drops of hydrochloric acid and add 1 ml in excess. Dilute to 100-150 ml, add 2-3 gm of tartaric acid and then add a 10 percent aqueous solution of sodium sulphite in 20-ml portions until, after standing on a steam bath for 20-30 minutes, the solution still smells of sulphur dioxide and is a pale yellow. Then with constant stirring, add dropwise from a burette, a 2 percent solution of potassium thiocyanate containing 2 percent sodium sulphite, until precipitation ceases. Add a threefold excess of reagent, boil, let stand for 10-15 minutes and filter through a No. 42 Whatman filter paper. Wash the paper and precipitate first with a solution containing 1 percent of potas-

sium thiocyanate and 1 percent tartaric acid and then with a 1 percent solution of ammonium sulphate. Discard the filtrate. Transfer the paper and precipitate to a porcelain crucible. Dry, char and ignite the paper. Take up in 3-4 ml of nitric acid, transfer to a clean beaker, dilute to 100 ml and boil to expel oxides of nitrogen. Add 3-4 ml of bromine water and boil until the excess bromine is expelled.

C. Titration

To the solutions from Section B above, add a slight excess of ammonium hydroxide and boil gently until the odour of ammonia is very faint, but still present. Add 7 ml of strong acetic acid. Cool to room temperature, add 3 gm of potassium iodide, dilute to 50-100 ml and titrate the liberated iodine with standard thiosulphate solution until the solution is nearly colourless. Add 2 gm ammonium thiocyanate (5) and swirl to dissolve. Finally add 2-3 ml starch solution and continue the titration to the end-point. Record the titration and calculate the copper content.

CALCULATIONS

For solids:

$$\% \text{ Cu} = \frac{\text{f} \times \text{t} \times 100}{\text{wt. sample, gm}}$$

For solutions:

$$\text{gm/l Cu} = \frac{\text{f} \times \text{t} \times 1000}{\text{aliquot taken, ml}}$$

where f = gm Cu per ml of thiosulphate
t = titration

If no titration is obtained, the results should be reported as "less than" the minimum amount detectable rather than using the term "not detectable". Assuming the minimum amount detectable with the weak standard of sodium thiosulphate is 0.0005 gm then the value to report would be given as:

$$\% \text{ Cu} = \text{less than } \frac{0.0005 \times 100}{\text{wt. sample, gm}}$$

or

$$\text{gm/l Cu} = \text{less than } \frac{0.0005 \times 1000}{\text{aliquot taken, ml}}$$

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The Volumetric Determination of Fluoride in Ores after Distillation as Fluosilicic Acid

METHOD F-1

SCOPE

The method is suitable for the determination of fluoride in uranium-bearing ores, concentrates and leach liquors.

RANGE

The method is intended for use with samples which contain more than 0.001% F.

OUTLINE

When an ore containing fluoride is treated with aqueous perchloric or sulphuric acid and subjected to steam distillation, the fluoride is evolved as hydrofluosilicic acid (1). The hydrofluosilicic acid is absorbed in a solution of sodium hydroxide. This solution, or a suitable aliquot, is titrated with thorium nitrate solution to an Alizarin Red S end-point after neutralizing the excess sodium hydroxide and buffering with chloroacetate buffer to provide a pH in the range 2.9 - 3.2 (2)

$$SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O \quad (1)$$

$$6\ NaOH + H_2SiF_6 \longrightarrow SiO_2 + 6\ NaF + 4\ H_2O \quad (2)$$

$$4\ NaF + Th(NO_3)_4 \longrightarrow 4\ NaNO_3 + ThF_4 \quad (3)$$

At the end-point, a lake of thorium and Alizarin Red serves as the indicator. So long as fluoride is in excess, it binds the thorium and the lake colour does not appear. There is a gradual change from yellow to pink and the end-point is not sharp, but so long as the titration is carried to the same colour change, reasonable reproducibility can be obtained. A blank determination is made and the correction applied.

Interference is caused by any substance capable of forming a slightly soluble compound or stable complex with fluoride or thorium. These include sulphate, arsenate, phosphate, excessive amounts of other halogen compounds, nitrates, uranium, aluminum, boron, silicon, iron, titanium, zirconium, alkaline earths, magnesium and the rare earths (3).

Willard and Winter concluded that volatilization as hydrofluosilicic acid from sulphuric or perchloric acid solution is the best procedure for removing fluorine from interfering substances (1). If perchloric acid is used, organic material should be absent or very low. Perchloric acid has the advantage over sulphuric acid that more soluble salts are formed.

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The presence of borates, boric acid or gelatinous silica retards the distillation and recovery may not be complete. In addition, chlorine may be evolved due to the decomposition of perchloric acid, excessive amounts of chloride or more particularly chlorate. Interference from chloride may be prevented by adding an excess of silver perchlorate to the still. The effect of chlorate may be partly overcome by adding excess ferrous sulphate before distillation is begun.

Distillation of fluorine from samples containing aluminum silicate is said not to be successful, but recoveries from solutions that contain aluminum ion are normal. The reviews by McKenna (4, 5, 6) provide considerable supplementary detail on this procedure.

APPARATUS

Fluoride distilling apparatus:	Ace Glass No. 3445.
Steam distillation flasks:	2 litre, round bottom.
Glas-Col heating mantles:	250 ml and 2000 ml.
Variable transformers:	Powerstat Type 116—Superior Electric Co., Bristol, Conn., USA.
Burette:	micro—5 ml.
Balance:	accuracy to ± 0.05 mg.
Distillation apparatus assembly:	rods, clamps.
Beakers:	
Pipettes:	
Volumetric flasks:	
Graduated cylinders:	

REAGENTS

Perchloric acid:	70-72% reagent grade.
Standard fluoride solution:	2.210 gm sodium fluoride per litre (1 ml = 1 mg F.).
Thorium nitrate:	0.1N (13.8 gm thorium nitrate tetrahydrate per litre) 1 ml ≑ 1.09 mg F. Standardize this solution against the standard fluoride solution using the same titration procedure as for samples, but omitting the distillation step. Distill one standard from time to time to check recovery.
Buffer:	9.45 gm monochloracetic acid and 2.00 gm sodium hydroxide per 100 ml.
Indicator:	0.05 gm sodium alizarin sulfonate (Alizarin Red S) dissolved in 100 ml water.
Hydrochloric acid:	12M, reagent grade.
Hydrochloric acid:	dilute 1 ml 12M HCl to 100 ml with water.
Sodium hydroxide, 0.5M:	2 gm in 100 ml.
Hydroxylamine hydrochloride, 10%:	50 gm $NH_2OH.HCl$ in 500 ml.

PROCEDURE

Transfer a 1- to 5-gm accurately weighed sample, or a 5- to 25-ml aliquot of a solution to a distilling flask. Add several glass beads to the flask. If the liquid sample aliquots are less than 25 ml, add sufficient water so that the volume of liquid in the flask is about 25 ml. Add 25 ml water to each of the solid samples. If the sample contains a large amount of chloride, add an excess of

silver perchlorate. If the sample contains chlorate, add an excess of ferrous sulphate. It may also be necessary in the final titration to add indicator solution after each addition of thorium nitrate solution in order to obtain an end-point, since the colour of the indicator may be bleached.

Connect the distilling apparatus and lubricate the glass joints with 70% perchloric acid. Place a 600-ml beaker containing dilute sodium hydroxide solution under the condenser so that the tip of the condenser is immersed in the solution.

Add 30 ml of 70-72% perchloric acid to the sample in the flask, and raise the temperature to about 125°C. When this temperature is reached, begin passing in steam and adjust the variable transformers so that a temperature of 135°C ± 5°C is eventually maintained. Do not allow the temperature to rise above 140°C since decomposition of the perchloric acid becomes more rapid and too much chlorine may be formed.

Continue the distillation until about 300-400 ml of distillate have been collected. Keep the solution in the receiver alkaline by the addition of more sodium hydroxide if necessary. When the distillation is completed, disconnect the steam supply and turn off the heating mantles. Remove the distilling connecting tubes, rinse the condenser with water and drain the rinsings into the receiver.

Transfer the distillate to a 500-ml volumetric flask and dilute to volume with water. Pipette a 100-ml aliquot into a 250-ml beaker, (a smaller aliquot may be taken and diluted to 100 ml), and add 8 drops of indicator solution. If chlorine is present, add 2 ml 10% hydroxylamine hydrochloride solution. Neutralize by adjusting with dilute hydrochloric acid or sodium hydroxide solution (pink colour discharged). Add 1 ml chloroacetate buffer and titrate with 0.1N thorium nitrate solution to a pink end-point. Carry out a blank determination on reagents and correct for it.

CALCULATIONS

Solid Samples:

$$\%\ \mathrm{F} = \text{Titration} \times \text{factor} \times \frac{\text{final dist. vol.}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

Solutions:

$$\text{gm/l F} = \text{Titration} \times \text{factor} \times \frac{\text{final dist. vol.}}{\text{aliquot taken}} \times \frac{1000}{\text{sample vol.}}$$

EXAMPLE A

1. Solid sample—weight 2.000 gm
2. The distillate is diluted to 500 ml and an aliquot of 100 ml taken for analysis
3. Volume of thorium nitrate solution for titration = 0.67 ml
4. " " " " " " blank = 0.02 ml
5. " " " " " " net 0.65 ml
6. 1 ml of thorium nitrate solution = 1.09 mg F.

Calculation:

$$\frac{0.65 \times 1.09 \times 500 \times 100}{2.000 \times 1000 \times 100} = 0.17_7\%\ \mathrm{F}.$$

EXAMPLE B

1. Liquid sample — volume = 25.0 ml.
2. Distillate diluted to 500 ml and an aliquot of 100 ml taken for analysis.
3. Volume of thorium nitrate solution for titration = 1.30 ml.
4. " " " " " " blank = 0.02 ml.
5. " " " " " " net 1.28 ml.
6. 1 ml of thorium nitrate solution = 1.09 mg F.

Calculation:

$$\frac{1.28 \times 1.09 \times 500 \times 1000}{25 \times 1000 \times 100} = 0.27_9 \text{ gm/l F.}$$

If no titration is obtained, the amount of fluoride should be reported as "less than" the limit of detection, (an actual figure based on the sample weight and volumes used) rather than using the term "not detected". The limit of detection may be taken as 0.2 ml of titrating solution, i.e. for 0.1N thorium nitrate, 0.2 mg F. The value to be reported in such a case would be e.g.:

$$\% \text{ F} = \frac{\text{less than } 0.2}{1000} \times 1.09 \times \frac{\text{final sol. vol.}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

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Determination of Free Acid or Basicity in Mill Solutions

METHOD F.A.-1

SCOPE

The procedure described will determine free acid or "basicity" in acid solutions (pH 4 or less) containing hydrolyzable ions such as uranium, thorium, iron, and aluminum (1). Acid complexes, such as are formed by arsenate and phosphate, are also broken up and titrated by this procedure, although the acid they contain may not actually be available for leaching (2). A correction for them may be made (2), (3) but this is beyond the scope of the method.

RANGE

The lower limit depends on the accuracy with which the end-point can be determined. With solutions containing only small amounts of hydrolyzable and other salts, the limit is about $\pm$ 0.2 gm/l H_2SO_4 (or $\pm$ 0.004 N H^+). With large amounts of such salts difficulty may be experienced with amounts less than $\pm$ 1 gm/l H_2SO_4 (or $\pm$ 0.02 N H^+). These figures also represent the probable error.

OUTLINE

Direct titration of the free acid content of the liquors used in ore-leaching is not possible due to the high concentration of hydrolyzable salts present in them. Examples of attempts at such titrations will be found in reference 1. By adding a neutral complex-forming reagent, such as potassium oxalate, stable complexes of uranium, thorium, iron and aluminum are formed which only hydrolyze at hydrogen ion concentrations below that at which all the free acid has been consumed. As a result an inflection corresponding to the consumption of the free hydrogen ion concentration is obtained when the complexed solution is titrated with standard potassium hydroxide solution. This inflection point is usually distorted and displaced by a variable amount, due to the high and varying content of salts in the solutions. Also, due to the weak ionization of oxalic acid, the pH change at the end-point is seldom more than 1 or 2 pH units. For this reason it is difficult to choose a suitable indicator for the system. By first plotting a curve and determining the end-point by one of the recommended methods, a number of similar solutions may be titrated using a pH meter or the Beckman Autotitrator. For critical work, a curve should be plotted or an instrument such as the Precision Dow Recordomatic Titrator used in every case. Both methods are described here.

APPARATUS

Precision Dow Titrimeter:

Warning: Carefully read the instruction manuals (4) (5) before attempting to turn on the unit.

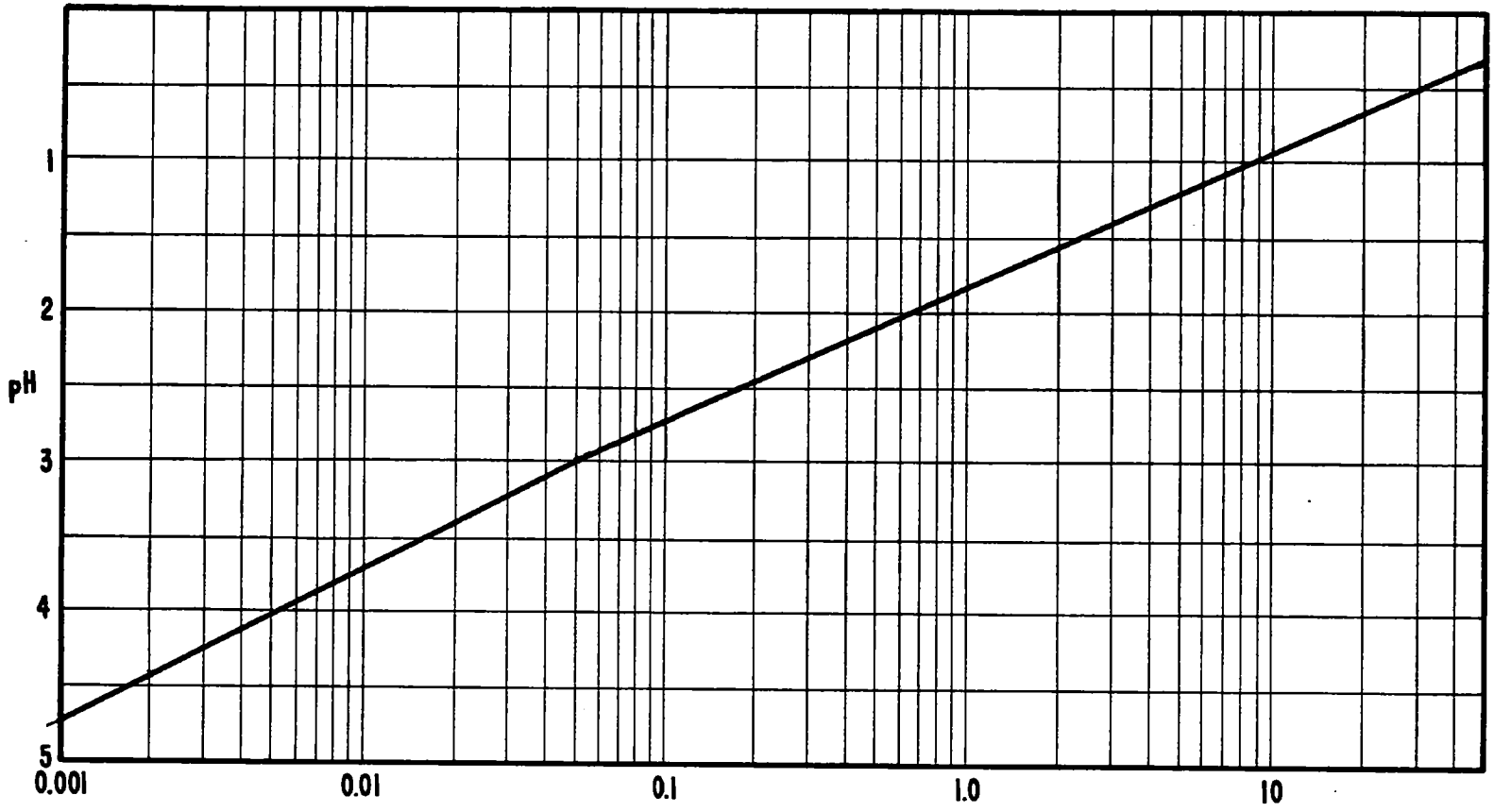

FIG. 1 - THEORETICAL H_2SO_4 GRAMS PER LITER

Beckman Autotitrator or Model G or H2 Beckman pH meter: Use only for routine samples where the end-point can be specified with some certainty. Carefully read the instruction manuals (7, 8) before using.

Glass electrode:

Saturated calomel electrode:

Graduated cylinder, 25 ml:

REAGENTS

Potassium oxalate solution: Dissolve 280 grams of $K_2C_2O_4$ in 1 litre of distilled water. Adjust to a pH of 8.5 with KOH or oxalic acid.

Potassium hydroxide solution, N/10: Dissolve a weight of reagent grade potassium hydroxide corresponding to 5.6 grams of KOH. Standardize against potassium biphthalate as follows: Weigh 0.5-1.0 gm portions of potassium acid phthalate into 200 ml Erlenmeyer flasks. Record the weight to the nearest mgm. Add 100 ml of water to each portion and shake until the solid has dissolved. Add 3 drops of phenolphthalein solution (0.1% in 1:1 v/v ethyl alcohol-water) and titrate with N/10 KOH until a pale pink colour is obtained.

$$\text{Then Normality} = \frac{\text{wt. of sample taken} \times 1000}{204.1 \times \text{titration}}$$

Note: 1 gram of potassium biphthalate will neutralize about 49 ml N/10 KOH.

Sulphuric acid solution N/10: Determine the normality by titration against the standard potassium hydroxide.

Standard buffer solutions: pH 4, 7, 10.

Kleenex: small size.

PROCEDURE

A. Using the Precision Dow Recordomatic Titrator

Check the pH of the solution as received. Determine the approximate free acid content from the chart in Figure 1, (solutions with pH 2 or greater are probably basic). Using this estimate, pipette accurately an aliquot that will give a KOH titration of 10-15 ml, if the pH is less than 1.5. Transfer to a 250-ml beaker containing 25 ml of 28% potassium oxalate solution. If the pH was 1.5 or greater, transfer a 10-ml aliquot to a 250-ml beaker containing 25 ml of 28% potassium oxalate and 25 ml of N/10 sulphuric acid.

In either case, make to about 100 ml with distilled water. If using the instrument for the first time, read the instruction manuals (4, 5) carefully. Turn the instrument on at least 2 hours before using. Place the N/10 KOH storage bottle on the instrument, clean out and fill the burette with N/10 KOH. Check the battery-life indicator to see if the batteries need changing. Standardize the instrument as described in the manual (page 4). Insert the glass and calomel electrodes and the burette delivery tip in the beaker cover. Turn the "Feed Pump Selector Switch" to the side being used. Set the "Scale Selector Switch" for the desired pH range (usually 4-14 for this titration). Re-adjust the zero and full scale settings, then adjust the recorder to give the correct pH on the scale, using standard buffer solutions. (Make sure the burette delivery tip does not enter the beaker of buffer, using e.g. a 100-ml beaker to give clearance.)

Rinse and dry the electrodes with Kleenex. Put the sample beaker in place. Turn the stirrer on, set the feed control at the desired speed, turn the "Zero Switch" to the correct side, note the chart "Volume" reading, and turn on the feed switch. Run about 2 ml past the inflection point, and turn off the feed. If the inflection is sharp, estimate the end-point visually. If it is not sharp estimate the inflection by the "Concentric Arcs" method (6).

Briefly the procedure is to determine the centre of curvature of each half of the inflection, using the scribed concentric arc template and to join these centres. The point where this line cuts the curve is the end-point.

Having determined the volume of the titration, calculate the acidity, or basicity as H_2SO_4 in grams per litre (*see* "Calculations").

B. Using the Beckman Model K Autotitrator

If using the instrument for the first time, read Bulletin 239 A (7) carefully before turning on the line switch.

Any of the regular glass electrode-calomel reference electrode assemblies may be used.

With a beaker of water on the beaker platform, turn the "Off-On" switch to "On". Let the instrument warm up for 5 minutes. Set the "pH-MV" switch to pH. Remove the beaker of water. Rinse the electrodes with distilled water, and wipe them off with Kleenex. Put a beaker of pH 7 buffer on the beaker platform. Raise it until the lower ends of the electrodes are immersed, but clear the titrating tip of the burette (i.e. do not let it come inside the beaker).

Turn the "Acid-Set-Base" switch to "Set". Adjust the "Temperature Compensator" to the temperature of the buffer. Turn the "Selector" Switch to correspond to the delivery unit being used. Rotate the "pH-MV" dial very slowly until the indicator light clicks on or off (depending on the direction of rotation). Set the zero point of the adjustable index directly over the pH reading of the "pH-MV" dial corresponding to the exact pH of the buffer (i.e. at the temperature of standardization as shown on the label of the buffer bottle). Remove the beaker of buffer solution and discard. Rinse the electrodes with distilled water and replace the beaker of distilled water.

Drawing a Titration Curve

If the Precision Dow Recordomatic titrator is not available for determining the exact end-point of the titration, draw up a curve using the procedure outlined on page 8 of the bulletin (7).

Titration Procedure

Place the beaker containing the solution on the beaker platform and raise into position. Adjust the "Temperature Compensator" to the temperature of the sample (°C). Set the "pH-MV" dial to "pH". Turn the "pH-MV" dial so that the pH value of the end-point, as determined from the pH titration curve of similar samples, is opposite the adjusted index line. Turn the selector switch to the position corresponding to the delivery unit to be used. Adjust the anticipation control, indicator electrode, and delivery tip as described on page 9 of the manual (7). Turn the "Acid-Set-Base" switch to "Acid", zero the burette (containing 0.1N KOH) and turn the "Delivery Unit" switch to "Titrate".

Prepare a second sample while the first is titrating and perform any calculations on previous samples.

When the unit stops titrating, read the burette, re-zero, remove the beaker and replace with the beaker containing the next sample to be titrated.

CALCULATIONS

1. Where 20 ml of sulphuric acid 0.1 N has been added,

$$\text{Free Acid (gm } H_2SO_4\text{/liter)} = (T-20) \times N \times \frac{49.04}{1000} \times \frac{1000}{\text{sample vol. taken}}$$

where T = titration volume used
N = normality of KOH solution.

If the amount of potassium hydroxide consumed is less than the amount of 0.1 N sulphuric acid added, the solution is basic insofar as free acid is concerned, and the result should be reported as "minus X grams per liter H_2SO_4".

2. Where no standard sulphuric acid was added,

$$\text{Free Acid (gm } H_2SO_4\text{/liter)} = T \times N \times \frac{49.04}{1000} \times \frac{1000}{\text{sample vol. taken}}$$

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8. Beckman Bulletin—190-C and 230-B.

The Colorimetric Determination of Total Iron and Ferric Iron with Ferron

METHOD Fe-1

SCOPE

This method is intended to be used for the determination of ferric and for total iron in solutions, and for the determination of total iron only in ores and solid samples.

To avoid confusion, the assay "ferrous iron" has been reserved for the determination by the dichromate oxidation method (6).

The following separate procedures are described:

A. *Solution Samples*
1. Ferric iron
2. Total iron (pure solutions)
3. Total iron (impure solutions)
   (a) H_2S — hydroxide separation (cobalt and nickel low)
   (b) H_2S — cupferron separation (cobalt and nickel high)

B. *Solid Samples*
1. Total iron
   (a) Ores high in silica, aluminum or phosphates
   (b) Oxidized or roasted ores
   (c) Sulphide and arsenical ores
   (d) Uranous phosphate precipitates
   (e) Diuranate precipitates

RANGE

From 0.005 gm/l in solutions and 0.005% in solids (based on a 10-ml and a 1-gm sample, respectively) i.e. from 0.05 mg to 0.5 mg in the final aliquot, using 1-cm cells. The range can be extended by using cells with longer light paths. An accuracy of 2% can be expected over this range.

OUTLINE

Ferron or 7-iodo-8 hydroxyquinoline-5 sulphonic acid has an orange-yellow colour in aqueous solutions. This becomes green in the presence of ferric iron, and is read at 645 mμ. The colour reaches a maximum in 5 minutes and does not fade on standing. The colour intensity is affected by the pH, but is constant and reproducible in the range of 2.5 $\pm$ 0.2. The pH is maintained in this range by the use of a hydrochloric acid-potassium biphthalate buffer.

The following ions interfere if present in more than the amounts given: citrate 5 mg; cyanide 0.2 mg; fluoride 0.2 mg; iodide 0.0 mg; orthophosphate 2 mg; oxalate 0.0 mg; pyrophosphate 0.0 mg; tartrate 25 mg; aluminum 1 mg; chromic 0.5 mg; chloroplatinate 4 mg; cobaltous 1 mg; cupric 0.02 mg; lead 10 mg; nickelous 0.1 mg; thorium 3 mg; and uranyl 10 mg; per 0.1 mg of ferric iron in the final aliquot i.e. cupric copper must be less than 20% of the ferric iron while uranium may be present up to 100 times the ferric iron content. Ferrous iron oxidizes slowly (2). Therefore solutions containing ferrous iron should be read within 5-10 minutes after the colour has been developed.

Thorium, rare earths, silver and lead are separated as chlorides and fluorides. Organic acids, cyanide, fluoride etc., are removed by fuming with perchloric acid. The heavy metals (copper, lead, platinum etc.) are precipitated with hydrogen sulphide, or thioacetamide. An ammonium hydroxide-ammonium chloride separation removes copper, silver, nickel and cobalt. (Two precipitations may be required if the nickel content is high.) A sodium hydroxide-carbonate-peroxide separation then removes uranium, aluminum, phosphate, chromate, tungstate and vanadate.

Alternatively, a cupferron extraction may be used to separate iron from cobalt, nickel, uranium, platinum, aluminum, lead, manganese, chromium, phosphate, fluoride etc. (copper and thorium if present, accompany the iron). Copper may then be removed by ammonium hydroxide as before, if necessary. This is the method of preference if the sample contains much nickel or cobalt.

Ferric iron in solutions is determined without separations to reduce as much as possible the possibility of oxidation of the ferrous iron. The only interfering ions liable to be present are fluorine, copper and nickel and they are not usually present in interfering amounts. If they are present, accurate results cannot be obtained by the procedure given.

APPARATUS

Beakers, Pyrex, Griffin low form:	250 ml.
Erlenmeyer flasks:	125 ml.
Platinum crucibles:	30 ml.
Funnels, filtering, and supports:	
Funnels, separatory:	250 ml.
Pipettes, volumetric:	1, 2 and 5 ml.
Flasks, volumetric:	50, 100 and 250 ml.
Spectrophotometer or filter photometer with 625-650 mμ filter:	
Glass or Corex cells, 1 cm light path:	
Steam bath:	
Refrigerated cooling bath:	Capable of giving approximately 5° C. One 14″ x 28″ x 12″ deep will provide space for 10 separatory funnels and for the chloroform and cupferron solutions.

REAGENTS

Hydrochloric acid:	
Hydrochloric acid, 5% solution:	
Hydrochloric acid, 10% solution:	v/v.

Sulphuric acid:	
Sulphuric acid, 1:1:	v/v.
Perchloric acid:	
Bromine water:	saturated.
Nitric acid:	
Ammonium hydroxide:	
Sodium hydroxide:	
Sodium hydroxide solution, 10%:	
Sodium hydroxide solution, 5%:	Add 0.05% sodium sulphate.
Hydrogen sulphide:	
Thioacetamide:	5% aqueous solution.
Ammonium chloride:	
Ammonium chloride solution, 2%:	
Hydrogen peroxide solution, 3%:	1 volume Superoxol diluted with 9 volumes of water.
Sodium carbonate:	
Potassium permanganate:	.01% aqueous solution.
Cupferron:	6% aqueous solution.
Chloroform:	
Ferron (7-iodo-8 hydroxyquinoline-5 sulphonic acid):	0.2% aqueous solution. Weigh 2 gm of Ferron into a litre volumetric flask, dilute to 1 litre and agitate thoroughly. Let stand for about 24 hours with occasional agitation and filter if necessary.
Buffer solution:	For four litres of buffer solution. Dissolve 40.84 gm of potassium biphthalate (MW204.22) in 2 litres of distilled water. Dilute 11 ml of concentrated hydrochloric acid (37-38%) to 2 litres. Mix the two solutions. The pH of this solution should be between 2.4 and 2.6.
Standard iron solution:	Dissolve 0.7020 gm of $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$ reagent in about 100 ml of distilled water. Add 5 ml of concentrated H_2SO_4 (iron free) and 5-10 ml of bromine water. Boil until all the iron is oxidized and the excess bromine expelled. Cool and dilute to 1 litre in a volumetric flask. Check the iron value by passing through a Jones reductor and titrating with $KMnO_4$ which has been standardized against Bureau of Standards sodium oxalate or with standard $K_2Cr_2O_7$ using diphenylamine indicator.

Preparation of Standard Curve

Pipette 5 ml of 0.2% Ferron into a suitable number of 50-ml volumetric flasks, add about 25 ml of buffer solution and mix. Pipette various aliquots of the standard ferric iron solution containing from 0.01 to 0.7 mg of ferric iron. Dilute to the mark with buffer solution and mix. Let stand for 10-15 minutes and read the transmittancy using 1-cm cells and a wave length of 645 mμ. Plot a graph of transmittancy vs. mg ferric iron on semi-logarithmic paper.

PROCEDURE

Preliminary Treatment

A. Solution Samples

1. *Ferric Iron*

Pipette an aliquot portion of the sample containing between 0.05 and 0.5 mg of ferric iron directly into a 50-ml volumetric flask and develop the colour as described below.

The accuracy of the determination depends upon the ratio of the interfering ions, listed under "Outline", to ferric iron. Ferrous iron oxidizes to a certain extent on standing and will therefore interfere. The rate of oxidation of ferrous to ferric is accelerated if oxidizing ions are present.

2. *Total Iron in Solutions Containing Insignificant Amounts of Interfering Ions*

Pipette an aliquot of the sample into a 125-ml Erlenmeyer flask, dilute to about 25 ml, add 2-3 ml of bromine water and boil off the excess bromine. If a precipitate forms add a few drops of hydrochloric acid, cool and filter (if necessary) into a volumetric flask. Dilute to the mark, shake well and determine the iron in an aliquot portion of this solution as outlined below.

3. *Total Iron in Solutions Containing Significant Amounts of the Interfering Ions*

(a) *Primary Method*—Pipette an aliquot of the solution into a 250-ml beaker, add 2-3 ml of hydrofluoric acid and 2-3 ml of hydrochloric acid. Evaporate to dryness at low heat. Moisten the residue with 1 ml of hydrofluoric acid, 1 ml of hydrochloric acid and 40-50 ml of water. Digest for a few minutes and filter off the insoluble fluorides and chlorides. Wash the paper and precipitate thoroughly with hot 1% hydrochloric acid.* Add 5 ml of 1:1 sulphuric, 5 ml of nitric and a few drops of perchloric acid to the above filtrate and evaporate just to dryness. Repeat the sulphuric-nitric-perchloric acid treatment a few times to remove interfering anions. Digest the residue in the beaker, with 85-90 ml of distilled water and 5 ml of hydrochloric acid until the soluble salts are in solution. Bubble H_2S through the solution for 15-20 minutes, or add a slight excess of a 5% aqueous solution of thioacetamide, and digest at 90°C. for 10-15 minutes. Filter through a No. 42 Whatman paper into a clean beaker. Wash the precipitate and paper with warm acidulated hydrogen sulphide water. Do not let the precipitate become dry. If the precipitate is large, place the original beaker under the funnel and dissolve it with aqua regia. Add 5 ml of 1:1 sulphuric acid to the beaker containing the dissolved sulphides and evaporate just to dryness. Dissolve the residue in 80-90 ml of distilled water and 5 ml of hydrochloric acid. Precipitate and wash the hydrogen sulphide metals as before. Discard the precipitate unless it is to be used for the determination of copper or bismuth. Combine the filtrates from the hydrogen sulphide separations and boil off the excess hydrogen sulphide. Evaporate the combined filtrates to about 100 ml, add 5-6 ml of bromine water or hydrogen peroxide and boil until the excess peroxide or bromine is expelled. Neutralize the solution with ammonium hydroxide (litmus), add 3-4 gm of ammonium chloride and heat for 4-5 minutes. Filter through a fast filter paper and wash the precipitate with hot 2% ammonium chloride solution. If nickel is high dissolve the precipitate in hot 5% hydrochloric acid and repeat the ammonium hydroxide separation. Discard the filtrates unless they are to be used for the determination of nickel, calcium or magnesium. Dissolve the precipitate in warm 5% hydrochloric acid, nearly

* Omit this step if the calcium or magnesium content is high. If *large* amounts of calcium or magnesium are present, the rare earths should be precipitated after the ammonium hydroxide or cupferron separations rather than at the start of the analysis. The fluoride ions should then be removed by evaporation of the filtrate with sulphuric or perchloric acid.

neutralize with a 10% sodium hydroxide solution and dilute to about 50-60 ml with distilled water. Pour the solution slowly and with constant stirring into a beaker containing 50 ml of 10% sodium hydroxide solution, 1-2 gm of sodium carbonate and 2-3 ml of 3% superoxol. Heat nearly to boiling and digest for 20-30 minutes. Filter through a medium filter paper which has been washed with a hot 5% solution of sodium hydroxide containing a little sodium sulphate. Wash the precipitate with the same solution. If the sample contains large amounts of aluminum and/or phosphate, dissolve the precipitate in hot 5% hydrochloric acid and reprecipitate the iron as before. Discard the filtrates. Dissolve the precipitate in hot 5% hydrochloric acid, add 2 ml of perchloric acid and evaporate just to dryness. Digest the residue with 20-25 ml of distilled water and 2-3 drops of hydrochloric acid until the soluble salts are in solution, cool, transfer to a volumetric flask and dilute to the mark. Determine the iron in an aliquot portion of this solution as outlined below.

(b) *Alternative Method for Removing Impurities*—Pipette an aliquot portion of the solution into a 250-ml beaker and carry out the procedure outlined in subsection 3 (a), up to the point when the hydrogen sulphide group has been removed. Boil off the hydrogen sulphide in the filtrate from the hydrogen sulphide separation, add 3-5 ml of hydrogen peroxide and boil off the excess. Adjust the acidity of solution to be 1:9 in hydrochloric acid, add a few drops of a weak potassium permanganate solution until the iron, uranium, etc., are oxidized and the solution turns pinkish. Cool the solution to about 5°C and transfer to a cold 250-ml separatory funnel. Add 2-3 ml portions of a cold 6% aqueous solution of cupferron until an excess of the reagent is present as indicated by the formation of a fine white precipitate which redissolves as contrasted to the flocculent insoluble cupferrate precipitate. Agitate after each addition of the reagent. Stopper the funnel and shake thoroughly. Release the vacuum in the funnel by temporarily inverting it and partially opening the stopcock. Remove the stopper, add 25 ml of cold chloroform, replace the stopper and shake thoroughly. Release the vacuum as before, remove the stopper and let the chloroform layer settle out. Drain off the chloroform layer into a clean beaker and repeat the chloroform extraction a few times, using 5-ml portions of chloroform until the chloroform layer is water white. Combine the chloroform extractions and evaporate nearly to dryness on a steam bath. Add 20-25 ml of nitric acid, 10 ml of 1:1 sulphuric acid, a few drops of perchloric acid, and evaporate to dryness. Repeat the acid digestion a few times if necessary until all the organic material is decomposed. Digest the residue with 20-25 ml of hot water, 2-3 drops of hydrochloric acid and a few drops of bromine water. Boil until the excess bromine is driven off. Filter, if necessary, into a volumetric flask, cool, dilute to the mark and determine the iron in an aliquot portion as outlined below.

B. Solid Samples

1. *Total Iron Only*

(a) *Ores etc. high in Silica, Aluminum and/or Phosphates, and low in Sulphides, Lead, Arsenic, Silver etc.*—Weigh 0.5 to 2 gm of the sample into a platinum crucible. Add about 5 gm of sodium carbonate and fuse over a burner. Cool, place the crucible in a beaker containing 100-125 ml of water and digest until the mass disintegrates. Filter and wash the residue a few times with hot water. Dissolve the residue in hot 5% hydrochloric acid and reprecipitate the iron, etc., with sodium hydroxide-carbonate-peroxide as above under subsection 3 (a). Discard the filtrates. Dissolve the precipitate in hot 5% hydrochloric acid and

precipitate the iron with ammonium hydroxide as above under subsection 3 (a). Dissolve the precipitate in hot 5% hydrochloric acid, add 1-2 ml of perchloric acid, evaporate to dryness and then digest the residue with 20-25 ml of water containing 2-3 drops of hydrochloric acid. Filter, if necessary, into a volumetric flask, cool, dilute to the mark, and determine the iron in an aliquot portion as outlined below.

(b) *Oxidized or Roasted Ores*—Weigh 0.5 to 2 gm of the sample into a 250-ml beaker, add 10 ml of water, 10 ml of hydrochloric acid and 5 ml of hydrobromic acid. Digest at a low heat for 10-15 minutes and then boil for 15-20 minutes. If the sample contains considerable magnetite or hematite add more water, hydrochloric and hydrobromic acid. Evaporate nearly to dryness, cool and cautiously add 5 ml of nitric acid. When the reaction subsides add 5 ml of water and 5 ml of perchloric acid. Evaporate to strong fumes, cover the beaker and reflux for 15-20 minutes to dehydrate the silica. Remove the cover, wash down the sides of the beaker and evaporate just to dryness at a low heat. Do not bake. Add 30-40 ml of 5% hydrochloric acid and heat until the soluble salts are in solution. Filter through a retentive filter paper into a clean beaker. Wash the residue a few times with hot 1% HCl and then with hot water. Examine the residue. If the residue is discoloured or large amounts of phosphate are present, transfer the filter paper and residue to a platinum crucible. Char and burn off the filter paper. Fuse the residue with about four times its weight of sodium carbonate. Cool, digest the melt in distilled water and filter through a medium filter paper (Whatman No. 30). Wash the paper and residue first with a warm 1% solution of sodium carbonate and then with hot water. Discard this filtrate. Place a clean beaker under the funnel and dissolve the residue in hot 5% hydrochloric acid, evaporate just to dryness, add 15-20 ml of hydrochloric acid and heat until the soluble salts are in solution. Filter, if necessary, wash the residue a few times with hot 1% HCl and finally with hot water. Combine this filtrate with the filtrate from the acid digestion. Remove the impurities as described under subsections 3 (a) or 3 (b), and determine the iron as described below.

(c) *Sulphide and Arsenical Ores*—Weigh 0.5 to 2.0 gm of the sample into a 250-ml beaker. Add 10-15 ml of water, 10-15 ml of nitric acid and 10-15 ml of bromine water. Let stand until the reaction subsides and evaporate just to dryness. Add 10 ml of water, 5 ml of hydrochloric acid, 3 ml of perchloric acid and evaporate just to dryness. Digest the residue with 30-40 ml of 5% hydrochloric acid until the soluble salts are in solution. Filter through a retentive paper into a clean beaker and wash the residue and paper with hot 1% hydrochloric acid. Examine the residue. If it is discoloured or large amounts of phosphate are present, fuse it with sodium carbonate and continue as in Section B, subsection 1 (b) above.

(d) *Uranous Phosphate Precipitates*—Weigh 0.5 to 5 gm of the sample into a 250-ml beaker. Dissolve the sample in 15 ml of water, 5-10 ml of nitric acid and 15-20 ml of hydrochloric acid. Evaporate to dryness. Wash down the sides of the beaker, add 5-10 ml of hydrochloric acid and evaporate just to dryness. Digest the residue in 30-40 ml of 5% hydrochloric acid until the soluble salts are in solution, filter and remove impurities as outlined under subsection 3 (b).

(e) *Diuranate Precipitates*—Weigh 0.5 to 5.0 gm of the sample into a 250-ml beaker. Add 100 ml of hot water, 3-5 gm of sodium carbonate and 3-5 ml of 3% hydrogen peroxide. Digest for 30-40 minutes and filter. Wash most of the precipitate back into the beaker and dissolve it in hydrochloric acid. Reprecipitate the iron with sodium hydroxide-carbonate-peroxide as outlined under subsection 3 (a). Filter and wash the precipitate a few times with hot water. Dissolve the

precipitate in hot 5% hydrochloric acid and precipitate the iron with ammonium hydroxide as outlined under subsection 3 (a). Filter and wash the precipitate with hot 1% ammonium chloride solution. Dissolve the precipitate in hot 5% hydrochloric acid, add 2-3 ml of 3% hydrogen peroxide and evaporate to dryness. Add 10-15 ml of water, 1 or 2 drops of hydrochloric acid and digest until the iron is in solution. Cool, transfer to a volumetric flask, dilute to the mark and determine the iron in an aliquot portion.

Volumetric Finish

If all the above separations have been carried out and the amount of iron is high it may be determined volumetrically. If titanium is present, stannous chloride (rather than the Jones reductor) should be used for reducing the iron. If vanadium is present it should be removed by a sodium hydroxide-carbonate-peroxide separation. (*See* METHOD Fe-3).

Colorimetric Finish

Pipette an aliquot portion of the solution, containing between 0.05 and 0.5 mg of ferric iron, into a 50-ml volumetric flask containing 5 ml 0.2% Ferron and 25 ml of buffer solution. Dilute to the mark with the buffer solution, shake, let stand 5-10 minutes and read the percent transmittancy using 1-cm cells and a wave length of 645 mμ. Determine the amount of ferric iron in the aliquot from the graph.

Table 1

Dilution Table for Iron Determination

Solutions

Range gm/l	1st Dilution Take ml	1st Dilution Dilute to ml	2nd Dilution Take ml	2nd Dilution Dilute to ml	Final Aliq. taken ml
0.01 – 0.05					5
0.05 – 0.10					2
0.1 – 0.3					1
0.3 – 2.0	5	50			2
2.0 – 7.0	2	100			2
7.0 – 15.0	2	250			2
15.0 – 25.0	5	100	5	50	2

Solids

Range %	1st Dilution Take gm	1st Dilution Dilute to ml	2nd Dilution Take ml	2nd Dilution Dilute to ml	Final Aliq. taken ml
0.01 – 0.05	5	100			10
0.05 – 0.1	5	100			5
0.1 – 0.5	2	100			2
0.5 – 1	1	100			2
1 – 5	1	250			2
5 – 10	0.5	250			2
10 – 20	0.5	250			1

CALCULATIONS

Solutions

$$\text{gm/l } Fe^{+++} \text{ (or Fe(total))} = \frac{\text{mg } Fe^{+++}/50 \text{ ml (graph)}}{1000} \times \frac{\text{2nd dil'n}}{\text{aliq.}} \times \frac{\text{1st dil'n}}{\text{aliq.}} \times \frac{1000}{\text{sample vol.}}$$

The above formula is applicable for total iron if all the iron has been oxidized.

Solids

$$\%\ Fe^{+++} \text{ (or Fe(total))} = \frac{\text{mg } Fe^{+++}/50 \text{ ml (graph)}}{1000} \times \frac{\text{2nd dil'n.}}{\text{aliq.}} \times \frac{\text{1st dil'n.}}{\text{aliq.}} \times \frac{100}{\text{sample wt.}}$$

If the sample gives approximately the same reading as the blank, the amount of iron should be reported as less than the minimum amount detectable (an actual figure based on the sample weight and volume used) rather than using the term "not detected".

The minimum amount detectable may be taken as 0.05 mg per 50 ml final dilution. The value to be reported is therefore:

$$\%\ Fe = \frac{<0.05}{1000} \times \frac{\text{2nd dil'n, ml}}{\text{aliq.}} \times \frac{\text{1st dil'n, ml}}{\text{aliq.}} \times \frac{100}{\text{sample wt.}}$$

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6. METHOD Fe-2:

Volumetric Determination of Total Iron, Reducing Power (Ferrous Iron) and Oxidizing Power (Excess Sodium Chlorate) in Uranium Leach Liquors—Rapid Mill Control Methods

METHOD Fe-2

SCOPE

These methods are intended for the rapid determination (by operating personnel) of the total iron content and of the presence or absence of a suitable excess of oxidizing agent (sodium chlorate) in sulphuric acid leach liquors, for process control purposes. The methods are simple to carry out and do not require any complicated equipment. They are not intended for accurate analysis since they are subject to important interferences, as discussed in the outline.

Since they are intended primarily as mill control methods, they are not ordinarily carried out in the Analytical Laboratory. To ensure that the analyses are carried out by the method desired, the following distinction is therefore made in requesting and reporting these analyses:

If the label and card request oxidizing power, reducing power or ferrous iron, analyses will be done by dichromate titration and will be reported as $NaClO_3$, or Fe^{++} as applicable.

If the label and card request total iron and/or ferric iron, the iron will be done colorimetrically, (METHOD Fe-1) or by the regular (precise) volumetric method (METHOD Fe-3), and reported as Fe or Fe^{+++}.

RANGE

The methods as outlined can be used to determine iron in the range 0.1 gm Fe/l and up and excess sodium chlorate in the range 0.1 gm $NaClO_3$/l and up.

OUTLINE

A. *Total Iron*

The method for total iron is the conventional one, consisting of the reduction of ferric iron to ferrous iron by means of stannous chloride in a strongly acid solution, followed by the oxidation of the excess stannous tin to the stannic form by mercuric chloride. The iron, which is all in the ferrous state is then titrated with a standard solution of potassium dichromate using sodium diphenylamine sulphonate as an internal indicator. No prior separations are employed.

The reactions are:

$$2\ Fe^{+++} + Sn^{++} \longrightarrow 2Fe^{++} + Sn^{++++}$$

$$Sn^{++} + 2\ HgCl_2 \longrightarrow Hg_2Cl_2 + Sn^{++++} + 2\ Cl^-$$

$$6\ Fe^{++} + Cr_2O_7^{--} + 14\ H^+ \longrightarrow 6\ Fe^{+++} + 2\ Cr^{+++} + 7H_2O.$$

Phosphoric acid is added before titration to lower the oxidation-reduction potential of the ferric-ferrous system, permitting the use of the diphenylamine sulphonate indicator. It also reduces the colour of the ferric ion making the titration somewhat easier to carry out.

In spite of statements to the contrary (1) uranium interferes in this determination. Tests carried out in this laboratory (2) (3) showed that as much as 80% of the uranium present would be titrated by this method if more than a trace of iron is actually present. The presence of phosphate makes the titration of uranium practically quantitative. The interference of uranium can be greatly reduced by carrying out the reduction at not more than 35°C, and carefully controlling the acidity at about 2 N (2). It is felt, however, that the conditions required are too critical for use in a mill method. In point of fact, the uranium factor is so large compared to the iron factor that in the solutions ordinarily encountered, the error due to uranium would amount at the most to 0.8 gm/l Fe, (for 2 gm/l U_3O_8) (1 ml N/10 $K_2Cr_2O_7$ = 5.5 mg Fe, 14.0 mg U_3O_8).

This is not usually large percentagewise, since the iron content of these solutions is generally over 5 gm/l.

Copper, gold, molybdenum, arsenic, antimony and tungsten are also stated to interfere. They are not common constituents of most uranium leach liquors. Vanadate is reduced to vanadyl by stannous chloride, but is not included in the potassium dichromate titration if diphenylamine sulphonate is used as indicator, since any vanadate formed colours the indicator, too (4).

B. *Reducing Power*

The term "reducing power" is used here to denote principally the ferrous iron content of leach liquors and is expressed in terms of ferrous iron. The method used is exactly the same as for total iron except that the initial reduction step (including destruction of excess stannous chloride) is omitted.

$$6\ FeSO_4 + K_2Cr_2O_7 + 7\ H_2SO_4 \longrightarrow 3\ Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7\ H_2O$$

As might be expected the method will include tetravalent uranium and trivalent vanadium, if present. Certain other commonly found elements, which interfere in the corresponding method using permanganate, (e.g. manganese) if much fluoride is present, may titrate in the dichromate method although the point does not appear to have been investigated. If the reducing power, calculated as ferrous iron, approaches the value found for total iron, using the volumetric method, tetravalent uranium (or trivalent vanadium, though this is not likely with Canadian ores), is indicated. In this case the reducing power will exceed the true total iron found by the colorimetric method.

The above notes are included as a guide in explaining lack of agreement between the volumetric and colorimetric results for total iron, reducing power and ferrous or ferric iron. The basic purpose of the reducing power determination is to ascertain how much sodium chlorate must be added to achieve some particular ferric-ferrous iron ratio, and therefore all the reductants titrated by the procedure must be taken into account in any case.

C. *Oxidizing Power*

The oxidizing power ($NaClO_3$) determination is carried out if the reducing power determination indicates that there are no substances present which reduce dichromate. This usually means that excess chlorate ion is present. A knowledge of the amount is a guide to the mill staff in deciding how much to reduce the chlorate addition to achieve the desired quantity. The procedure

consists of adding a known amount of ferrous sulphate, sufficient to provide an excess over that required to reduce the chlorate, then back-titrating the excess with the standard dichromate solution.

$$NaClO_3 + 6\ Fe\ SO_4 + 3\ H_2SO_4 \longrightarrow 3\ Fe_2(SO_4)_3 + 3\ H_2O + NaCl$$

$$6\ Fe\ SO_4 + K_2Cr_2O_7 + 7\ H_2SO_4 \longrightarrow 3\ Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7\ H_2O$$

Vanadate and chromate, if present would be expected to interfere. Chromium is seldom found in Canadian acid leach liquors except in trace amounts, usually derived from attack of stainless steel equipment. Ores from the Beaverlodge area contain small amounts of vanadium, which is dissolved in acid leaching. On the basis of U.S. experience, where the E.M.F. of a solution is more negative than −0.70 volts (Pt electrode vs saturated calomel half-cell), vanadate (V^5) ion will be present (5). As with the ions interfering in the reducing power determination, however, the interference is actually of no moment. The results obtained are interpreted in the light of leaching and ion-exchange performance, and the quantitative adjustments made in terms of the results of the titrations.

APPARATUS

Beakers, Griffin Pyrex:	250 ml.
Pipettes:	5, 10, 25 ml.
Burette:	25 ml.
Dropping bottles:	60 ml or 120 ml sizes, for dispensing stannous chloride, mercuric chloride and diphenylamine sulphonate.
Graduated cylinders:	10 ml, 30 ml.
Small water bath:	
Hot plate:	

REAGENTS

Hydrochloric acid, concentrated, CP:	
Sulphuric acid, concentrated, CP:	
Sulphuric acid 1:1:	WEAR GOGGLES: Cautiously, with stirring, add 500 ml concentrated sulphuric acid to 500 ml water in a 2000 ml beaker, allowing the solution to cool between each addition. When the acid has been added, adjust the volume to 1 litre.
Phosphoric acid, 85%, CP:	
Standard potassium dichromate solution, N/10:	Weigh out 4.904 grams of dried $K_2Cr_2O_7$, dissolve in water and dilute to 1 litre in a volumetric flask. 1 ml = 0.0056 gm Fe: 0.014 gm U_3O_8: 0.0018 gm $NaClO_3$.
Stannous chloride solution, 5%:	Dissolve 50 gm $SnCl_2 . 2H_2O$ in 100 ml of concentrated hydrochloric acid and dilute to 1 litre. Add a few pieces of metallic tin and store in a dark bottle.
Mercuric chloride solution, saturated:	About 70 grams of $HgCl_2$ in 1 litre of water. Store in a dark bottle.

Diphenylamine indicator: Dissolve 1.6 gm of barium diphenylamine sulphonate in 500 ml of water containing 5 ml of concentrated sulphuric acid. Let the barium sulphate formed settle out and decant or filter off the supernatant liquid.

Ferrous sulphate, 0.2N: Dissolve 55.6 grams $FeSO_4 . 7H_2O$ in 500 ml of water, add 50 ml of concentrated sulphuric acid, and cool. Filter through a rapid filter paper or glass wool, into a 1 litre volumetric flask, dilute to the mark and store in a dark bottle. Standardize against the standard potassium dichromate solution and express in terms of this solution i.e. 1 ml of ferrous sulphate solution = X ml of 0.1N potassium dichromate solution. The factor, "X" is used in calculating the "Dichromate Equivalent" of the ferrous sulphate added in the "Oxidizing Power Determination".

PROCEDURE

A. *Total Iron*

Pipette an aliquot portion of the solution (*see* Table 1) into a 250-ml beaker. Dilute to 50 ml. Add a few drops of concentrated hydrochloric acid and heat nearly to boiling. Remove from the hot plate. Add stannous chloride dropwise until the solution is just colourless, then add one or two drops in excess. Be careful not to add more than two drops excess over the amount required to decolourize the iron. Cool the solution (in a water bath), dilute to 75 ml with water, and then, while stirring, pour 10 ml of saturated mercuric chloride solution into the beaker.

Add 10 ml of 1:1 sulphuric acid, 5 ml of concentrated phosphoric acid and 2 drops of diphenylamine indicator.

Titrate with standard potassium dichromate to the purple end-point and record the titration in ml.

Table 1

Suggested Aliquots of Sample Solution

Estimated Fe content gm/l	Aliquot ml
1–5	25
5–10	10
10–15	5

Calculate the titration in terms of Fe and report the result as total iron (dichromate titration) Fe, gm/l. (*See* "Calculations"—Total Iron.)

B. *Reducing Power*

Note: Reducing power determinations should be carried out as soon as possible after the sample is received, since air oxidation of ferrous iron can be rapid, particularly if fluoride or phosphate ion is present.

Pipette an aliquot portion (*see* Table 1) into a 250-ml beaker. Add 10 ml of 1:1 sulphuric acid and dilute the solution to 100 ml with water. Add 5 ml of phosphoric acid and 2 drops of diphenylamine sulphonate indicator.

Titrate with standard N/10 potassium dichromate solution to a purple end-point. If the ferrous iron content is being maintained at less than 1 gram per litre, N/20 potassium dichromate may be used. Carry out a blank

determination using 100 ml of water and adding all the reagents. Deduct this blank titration from the sample titration, and calculate the reducing power as Fe. Report the result as reducing power (Fe^{++}, gm/l).

C. *Oxidizing Power*

Pipette an aliquot portion into a 250-ml beaker. Add 10 ml of 1:1 sulphuric acid, and dilute to 50 ml. Add a drop of diphenylamine sulphonate indicator. If the solution turns purple, chlorate may be present. If the solution does not turn purple, chlorates are absent.

If the solution turns purple, add a measured amount of standard N/10 ferrous sulphate solution from a burette to reduce all the chlorates present, plus a 2-3 ml excess (10-15 ml total is usually sufficient if the proper aliquot is taken for the chlorate concentration range of the solution).

Heat the solution just below boiling for 15 minutes. Cool, add 5 ml of phosphoric acid and 2 drops of diphenylamine sulphonate indicator. Titrate with standard N/10 potassium dichromate solution to the purple end-point.

If only an occasional determination is required, the dichromate equivalent of the standard ferrous sulphate solution may be determined simultaneously with the sample titration. Transfer the same volume of the ferrous sulphate solution used for the sample, to a second 250-ml beaker. Dilute and continue the procedure in the same manner as with the sample. This titration is the "dichromate equivalent" of the ferrous sulphate, and is used in calculating the oxidizing power, as given under "Calculations". The dichromate equivalent of the standard ferrous sulphate solution may also be calculated using the factor determined by the procedure given under "Reagents", as $V \times X$ where V is the volume of the ferrous sulphate solution added to the sample.

Table 2

Suggested Aliquots of Sample Solution, Oxidizing Power Determination

Estimated Sodium Chlorate Content gm/l $NaClO_3$	Sample Solution Aliquot, ml
0.1–2	10
2–5	5

CALCULATIONS

A. *Total Iron*

$$\text{gm/l Fe} = \frac{T_1 \times 0.0056 \times 1000}{\text{sample aliquot taken, ml}}$$

B. *Reducing Power*

$$\text{gm/l } Fe^{++} = \frac{(T_1 - \text{blank}) \times 0.0056 \times 1000}{\text{sample aliquot taken, ml}}$$

C. *Oxidizing Power*

$$\text{gm/l } NaClO_3 = \frac{(T_2 - T_1) \times 0.0018 \times 1000}{\text{sample aliquot taken, ml}}$$

where T_1 = titration, ml N/10 $K_2Cr_2O_7$

T_2 = dichromate equivalent of $FeSO_4$ added.

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The Volumetric Determination of Iron in Ores and Mill Products

METHOD Fe-3

SCOPE

The method is applicable to all ores, solutions and precipitates.

RANGE

From 5 to 150 mg of iron can be determined with an accuracy of about ± 0.2 percent.

OUTLINE

Iron can be determined volumetrically by titrating a solution in which it has been reduced to the ferrous state, with a standard solution of potassium dichromate.

$$K_2Cr_2O_7 + 6\,FeCl_2 + 14\,HCl \longrightarrow 6\,FeCl_3 + 2\,KCl + 2\,CrCl_3 + 7H_2O$$

The end-point is detected with sodium diphenylamine sulphonate as an internal indicator, using phosphoric acid in the solution to lower the redox potential of the ferric-ferrous system into the range of this indicator. Phosphoric acid also reduces the colour of the iron, making the end-point easier to detect.

A trace of ferric iron must be present to catalyze the oxidation of the indicator. This is, of course, produced during the course of the titration, but if small amounts of iron are being titrated, it is well to add a little ferric chloride at the start so that the end-point will not be overshot due to the slowness of the indicator change.

Reduction is accomplished by means of an excess of a hydrochloric acid solution of stannous chloride

$$2\,FeCl_3 + SnCl_2 \longrightarrow 2\,FeCl_2 + SnCl_4.$$

The excess stannous chloride is then oxidized by mercuric chloride

$$SnCl_4 + 2\,HgCl_2 \longrightarrow SnCl_4 + Hg_2Cl_2\downarrow.$$

The mercurous ion formed is not titrated by dichromate (1, 2, 3, 4, 5).

The Jones reductor may also be used to reduce the iron (2), but this does not form part of the present method.

Other elements that can be reduced by stannous chloride and titrated with potassium dichromate interfere. These include uranium, copper, arsenic, antimony, molybdenum, tungsten and gold. Of these, uranium deserves special mention because it has been stated (2) that it does not interfere in the determination. Tests carried out here have shown that it is practically quantitatively

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titrated, particularly if phosphate is present (6, 7). Vanadium does not interfere, for while it is reduced by stannous chloride to vanadyl, it is not included in the dichromate titration because of the high redox potential of the vanadate-vanadyl system (8).

Of the interfering ions, tungsten (along with vanadium, chromium and phosphate) and most of the arsenic, antimony and uranium, are removed with a sodium hydroxide-hydrogen peroxide or sodium carbonate-hydrogen peroxide separation. Copper, lead, platinum, bismuth and the remainder of the arsenic, antimony and chromium are removed with a hydrogen sulphide separation. Any manganese present is first reduced with sodium sulphite to prevent it oxidizing the hydrogen sulphide and liberating sulphur. It also reduces arsenic and antimony, which, while not essential, speeds up the precipitation. The excess sulphur dioxide must itself be removed by boiling to prevent it interacting with the hydrogen sulphide and again liberating sulphur.

Zirconium, hafnium and titanium and part of the manganese and nickel are removed by an ammonium sulphide-ammonium tartrate separation. This separation also removes the remainder of the uranium. The remainder of the manganese, nickel and cobalt is removed by an ammonium hydroxide separation. Fluorine if present is removed by fuming with sulphuric acid. This step is done near the start of the analysis to prevent the co-precipitation of interfering elements as fluorides. Double separations are carried out when large amounts of the interfering elements are present or when a higher degree of accuracy is desired.

Many iron minerals can be brought into solution using acid attack. Magnetite and argillaceous hematite are almost completely decomposed by hydrochloric acid, although the white residue left may not be entirely free of iron. For sulphides and arsenides, and for certain complex ores, alkali fusion may be preferred, since by extracting the melt with water containing hydrogen peroxide, the iron is at the same time separated from sulphur, arsenic, phosphorus, vanadium, molybdenum, and some of the uranium, chromium, titanium and earth acids.

In general, however, the use of an initial acid attack followed by fusion of the residue is preferable wherever possible, since it results in less attack on the platinum crucible.

The procedures described below can also be used to purify iron for determination by methods other than volumetric. Thus, iron in small quantities can be determined colorimetrically on the solution of the ammonium hydroxide precipitate, using o-phenanthroline after reduction with hydroxylamine, or using "Ferron" after oxidation with hydrogen peroxide (METHOD Fe-2). The determination can also be completed gravimetrically by ignition of the ammonium hydroxide precipitate in the case of larger amounts. This, however, requires double precipitations including a double ammonium hydroxide separation.

APPARATUS

Beakers, Griffin low form:	250 ml, 400 ml size.
Pipettes:	5, 10, 25 and 50 ml sizes.
Flasks, volumetric:	250 ml, 500 ml, 1000 ml sizes.
Platinum crucibles:	25 or 30 ml.
Crucible tongs:	
Beaker tongs:	Fisher No. 2-620.
Filtering funnels:	long stem 65 and 75 mm dia.

Burettes:	50 ml size.
Reagent bottles:	
Dropping bottle:	25-30 ml capacity.
Burette support and holder:	Fisher No. 14-688.
Burner, Meker (for type of gas used):	
Tripod, iron:	Fisher No. 15-300.
Triangles:	Fisher No. 15-265 or 15-280.
Filter paper:	Whatman Nos. 41H, 30 and 42; sizes 11 and 12.5 cm.

REAGENTS

Hydrochloric acid, concentrated:	
Hydrochloric acid, dil.:	1:1 v/v.
Nitric acid, concentrated:	
Sulphuric acid, concentrated:	
Sulphuric acid, dil.:	1:1 v/v.
Perchloric acid:	
Hydrobromic acid:	
Phosphoric acid:	
Sodium sulphate:	
Hydrofluoric acid:	
Sodium hydroxide, pellets:	
Sodium carbonate:	
Potassium pyrosulphate:	
Bromine:	
Bromine water:	A saturated solution of bromine in distilled water.
Hydrogen peroxide, 30 percent:	
Stannous chloride:	
Stannous chloride solution:	Dissolve 50 gm of $SnCl_2 \cdot 2H_2O$ in 100 ml of hot HCl, dilute to 1 litre with distilled H_2O. Add a few pieces of metallic tin and store in a dark bottle.
Mercuric chloride solution:	A saturated solution of $HgCl_2$ in distilled H_2O. Store in a dark bottle.
Ammonium salt wash solution:	Add 5 ml of NH_4OH and 5 gm of $(NH_4)_2SO_4$ to 500 ml of water. Gas for 5 minutes with H_2S. Add a few drops of NH_4OH and mix.
Hydrogen sulphide:	
Thioacetamide:	
Ammonium sulphate:	
Tartaric acid:	
Ammonium hydroxide:	
Potassium dichromate:	Primary standard.
Potassium dichromate solution N/10:	Dissolve 4.9038 gm of $K_2Cr_2O_7$ in distilled water and dilute to 1 litre in a volumetric flask. If pure $K_2Cr_2O_7$ is used and the reagent is accurately weighed and diluted, it does not need to be standardized. If desired, the solution may be standardized against pure iron wire or against a Bureau of Standards iron ore. The $K_2Cr_2O_7$ should be dried at 105° C for 1 hour before weighing. 1 ml of N/10 potassium dichromate = 0.005584 gm iron.

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Potassium dichromate solution N/20: Dissolve 2.4519 gm of pure dry potassium dichromate in distilled water and dilute to 1 litre. Standardize if desired against pure iron wire or against a Bureau of Standards iron ore. 1 ml = 0.002792 gm iron.

Diphenylamine indicator: Dissolve 1.6 gm of barium diphenylamine sulphonate in 500 ml of distilled water and add 5 ml of sulphuric acid. Let the barium sulphate settle and decant through a Whatman No. 42 filter paper. Store in a dark reagent bottle.

Ferric chloride catalyst solution: 5 gm $FeCl_3$ and 6 ml concentrated sulphuric acid to 100 ml with water.

PROCEDURE

A. Decomposition and Preliminary Treatment

1. *Solid Samples*

(a) *Ores, Residues, Precipitates and Alloys*—Weigh out 0.5 to 2.0 gm of the sample (containing 40 to 150 mg Fe) and transfer to a 250-ml beaker. Add 15 to 20 ml of water, 15-20 ml of hydrochloric acid and 5-10 ml of hydrobromic acid. Heat to boiling and boil for 15-20 minutes. Cool, cautiously add 10 ml of 1:1 sulphuric acid and evaporate to strong fumes of sulphur trioxide. Cool and wash down the sides of the beaker. If the sample contains appreciable amounts of magnetite or arsenic, repeat the hydrochloric-hydrobromic treatment and again evaporate to strong fumes of sulphur trioxide. Cool, wash down the sides of the beaker, add 5-10 ml of nitric acid and evaporate until most of the free acid is expelled. Cool, wash down the sides of the beaker and evaporate just to dryness. Do not bake. Cool, add 30 ml of distilled water, 5 ml of 1:1 hydrochloric acid and 2-3 ml of 3% hydrogen peroxide. Digest until the soluble salts are in solution and filter through a No. 30 Whatman filter paper. Wash the residue thoroughly with a hot 1% hydrochloric acid wash solution and then with hot water. Reserve the filtrate. Transfer the residue and paper to a platinum crucible. Dry, char and ignite the paper and residue. Moisten the residue in the platinum crucible with a few drops of 1:1 sulphuric acid, add 4-5 ml of hydrofluoric acid and evaporate to dryness to volatilize the silica. Repeat this treatment if the amount of silica is high. Fuse the residue in the crucible with a little sodium carbonate or potassium bisulphate. Transfer the crucible and melt to the original beaker and digest the melt with weak hydrochloric acid. Filter through a No. 30 Whatman filter paper into the beaker containing the reserve filtrate. Discard the residue. Nearly neutralize the filtrate with a 5 percent solution of sodium hydroxide and dilute to 50-75 ml.

(b) *Ores, Residues and Precipitates, Low in Magnetite*—Weigh 0.5 to 2.0 gm of the sample (containing 40 to 150 mg Fe) into a platinum crucible. Add about five times as much sodium carbonate as ore and mix thoroughly. Cover with sodium carbonate and about one-half gm of potassium nitrate. Fuse over a burner until the sample is decomposed. Cool, transfer the crucible and contents to a 250-ml beaker and digest the melt with water containing 1-2 ml of hydrogen peroxide until the melt is thoroughly disintegrated. Filter through a No. 41 H filter paper and wash with a hot 1 percent sodium carbonate wash solution. Discard the filtrate and washings. Wash most of the precipitate back into the original beaker and dissolve the precipitate with hydrochloric acid. Dilute to 50-60 ml and nearly neutralize the solution with a 5 percent solution of sodium hydroxide.

2. *Solution Samples*

Pipette an aliquot containing 40 to 150 mg iron into a 250-ml beaker. Add 5-10 ml of nitric acid and 5 ml of 1:1 sulphuric acid. Evaporate to heavy fumes to

destroy any organic matter. Cool, dilute to 50 to 75 ml, and digest to redissolve the material. Nearly neutralize the solution with a 5% solution of sodium hydroxide.

B. Separations

Slowly pour the solution into a 400-ml beaker containing 50-60 ml of hot water, 5 gm of sodium hydroxide, 5 gm of sodium carbonate and 2-3 ml of hydrogen peroxide. Digest on the hot plate for 15-20 minutes and filter through a No. 41 H Whatman filter paper. Wash the precipitate with a 1 percent sodium hydroxide: 1 percent sodium sulphate wash solution. Discard the filtrate and washings. Wash most of the precipitate back into the beaker. Dissolve the precipitate with hydrochloric acid, reprecipitate and wash as outlined above. Discard the filtrate and washings. Dissolve the precipitate in 100 ml of 10 percent hydrochloric acid and neutralize the solution with ammonium hydroxide until the precipitate which forms dissolves with difficulty. Clear with a few drops of hydrochloric acid. Add 1 gm of sodium sulphite and boil until all the excess sulphur dioxide is expelled. Dilute to 150 ml, add 5-7 ml of hydrochloric acid, and 5-6 gm of tartaric acid. Heat just to boiling and bubble H_2S through the solution until the copper group is precipitated. Dilute to about 200 ml and continue bubbling gas through the solution for 10-15 minutes. Filter through a No. 42 Whatman paper into a 400-ml beaker. Wash the precipitate with slightly acidulated hydrogen sulphide wash solution (1% hydrochloric acid solution saturated with hydrogen sulphide). Reserve the filtrate and washings. If the amount of precipitated sulphides is high, dissolve them from the paper with a 10% nitric acid solution containing about 5 ml of bromine water. Wash the paper with hot water. Catch the filtrate and washings in the original beaker, add 10 ml of 1:1 sulphuric acid and evaporate just to dryness. Dissolve the residue with 100 ml of 5 percent hydrochloric acid solution and reprecipitate the sulphides as before. Filter and wash the precipitate as above into the beaker containing the reserve filtrate. Discard the precipitate. Neutralize the reserved filtrate with ammonium hydroxide and add 2-3 ml excess. Gas with hydrogen sulphide for a few minutes and warm to coagulate the precipitate. Cool, filter through a No. 30 Whatman paper and wash the precipitate with ammonium salt wash solution. Discard the filtrate and washings. If the precipitate is large or if large amounts of manganese, uranium or titanium are present it is advisable to repeat the ammonium sulphide-tartrate separation. In this case dissolve the precipitate in 100 ml of 5 percent hydrochloric acid and wash the paper with distilled water. Catch the filtrate and washings in the original beaker, add 2 gm of tartaric acid and bubble hydrogen sulphide through the solution for 10-15 minutes. Neutralize the solution with ammonium hydroxide, add 2-3 ml excess and continue passing hydrogen sulphide through the solution for 3-4 minutes. Warm to coagulate the precipitate. Cool, filter and wash the precipitate thoroughly with the ammonium salt solution. Discard the filtrate and washings. Dissolve the precipitate with 10-15 ml of 1:1 sulphuric acid plus 1-2 ml of nitric acid. Wash the paper with a little water. Catch the filtrate and washings in the original beaker, add 5 ml of nitric acid and evaporate to heavy fumes to destroy any remaining tartaric acid. Cool, dilute with 100-150 ml of distilled water and heat until the soluble salts are in solution. Add 5-6 gm of ammonium chloride and neutralize with ammonium hydroxide. Add a small excess. Heat to coagulate the precipitate and filter through a No. 41 H paper. Wash the precipitate with hot water. Discard the filtrate and washings. Dissolve the precipitate in 20-30 ml of 5 percent hydrochloric acid.

C. Reduction and Titration

Heat the sample solution and add stannous chloride solution dropwise with stirring until the greenish yellow colour just disappears. Add 1-2 drops excess, cool and rapidly add 20 ml of mercuric chloride. Dilute to 100-125 ml with distilled water, add 10 ml of 1:1 sulphuric acid and 5 ml of phosphoric acid. Add 3-4 drops of diphenylamine indicator (and if the amount of iron is small, 1 ml of ferric chloride catalyst solution) and titrate with standard potassium dichromate solution to the violet-blue end-point. Near the end-point the solution will become green and then blue-green or in the presence of large amounts of iron, a greyish blue. At this point, add the dichromate dropwise until the end-point is reached. An over-titration may be avoided by first titrating the solution, without phosphoric acid to the dark green colour (1.5 percent before the end-point), then adding the phosphoric acid and titrating to the end-point. Record the volume of the titration in ml, note the normality of dichromate solution used, and calculate as Fe.

CALCULATIONS

$$\% \text{ Fe} = \frac{T \times N \times 55.84 \times 100}{1000 \times \text{wt. sample}}$$

$$\text{gm/l Fe} = \frac{T \times N \times 55.84 \times 1000}{1000 \times \text{aliquot used}}$$

T = titration, ml

N = normality of potassium dichromate.

If no titration is obtained, the results should be reported as "less than" the minimum amount detectable, rather than using the term "not detectable". The minimum amount detectable with N/20 potassium dichromate may be taken as 0.00028 gm, and the value to report would be given as

$$\% \text{ Fe} = \text{less than } \frac{0.00028 \times 100}{\text{wt. of sample}}$$

$$\text{gm/l Fe} = \text{less than } \frac{0.00028 \times 1000}{\text{aliquot used}}$$

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The Determination of Iron in Uranium-bearing Materials using Ethyl Acetate Extraction and Colorimetric Bathophenanthroline Finish

METHOD Fe-4

SCOPE

This method is designed primarily for use on uranium-bearing materials containing very small amounts of iron. Samples containing larger quantities of iron should be analyzed by the ferron colorimetric (1, 2) or dichromate titration methods (3), although the ethyl acetate extraction as described here may be used as a preliminary step before either of these finishes.

RANGE

Iron determinations between 0.001% and 0.1% for solid samples and 0.001 gm/l to 0.1 gm/l for solution samples should be carried out by this method.

OUTLINE

The reagent 4,7-diphenyl-1,10-phenanthroline (bathophenanthroline) forms a coloured complex with ferrous iron which has been made the basis of a colorimetric procedure (4). This reagent is a new, substituted 1:10-phenanthroline which shows a great sensitivity towards iron. The molar extinction coefficient of the ferrous bathophenanthroline ion has been given as 22,400, which is considerably greater than that of 11,100 shown by ferrous 1:10-phenanthroline (4). This new reagent also presents the advantage of forming a complex which is extractable from aqueous solutions with certain immiscible solvents such as isoamyl alcohol. The pH range for optimum complex formation is wide, ranging from approximately 2 to 7.

Although bathophenanthroline is almost specific for iron, some interference has been found from copper. A general separation method is described for extracting iron from most contaminants by ethyl acetate extraction from strong (6. 5N) hydrochloric acid solution (5). This procedure is a modification of the standard diethyl ether extraction of iron from hydrochloric acid solution (6). The actual partition coefficient has been found to vary from 10 to > 100 depending on the iron concentration, being a maximum in 6.5N hydrochloric acid at about 10 gm/l total iron in the aqueous solution taken for extraction. To give an example, it has been found possible to extract with about 99% efficiency, 20 milligrams of iron from 6.5N hydrochloric acid solution using one extraction with 35 ml of ethyl acetate. It was found also that iron can be efficiently removed from the organic layer by water stripping. The water strippings can then be used directly for iron determination by the Ferron colorimetric method or dichromate titration method. This extraction will separate iron from copper and also from a number of other contaminants which would interfere with finishes

other than the bathophenanthroline procedure (2, 3). Arsenic and molybdenum are extracted by ethyl acetate under the conditions described in this procedure, but neither of these contaminants would be expected to interfere with either the bathophenanthroline (4, 5) or ferron methods (2).

A discussion of solvent extraction theory will be found in the outline of METHOD U-4, (this manual).

APPARATUS

Spectrophotometer, Beckman Model "B":	with 1 cm matched cells.
Separatory funnels, Squibb pear-shaped:	60, 125 and 250 ml.
Rubber stoppers, No. 0 and No. 1:	(for the separatory funnels)
or	Boil twice in ethyl acetate, 10 minutes each time.
Polyethylene stoppers:	
Volumetric flasks:	25 to 1000 ml.
Pipettes:	1 to 25 ml.
Centrifuge:	(and appropriate centrifuge tubes).
pH meter, Beckman H-2:	

REAGENTS

Bathophenanthroline solution 0.001M:	Dissolve 0.0835 gm of bathophenanthroline in 125 ml of 95% ethyl alcohol and dilute to 250 ml with distilled water.
Hydroxylamine hydrochloride (iron-free) solution, 10%:	Dissolve 25 gm of hydroxylamine hydrochloride in distilled water and transfer to a 125 ml or 250 ml separatory funnel, supplied with a glass stopper. Adjust the pH to 3.5-4.0 with 1N sodium hydroxide solution, add 5 ml of the bathophenanthroline solution and mix thoroughly. Add 10 ml of isoamyl alcohol and shake the mixture for about 30 seconds. Drain off the aqueous layer into a second separatory funnel and repeat the extraction until the organic layer is colourless. Give the iron-free aqueous layer an extra wash with isoamyl alcohol to remove any remaining bathophenanthroline reagent and dilute the aqueous layer to 250 ml with distilled water. Make this solution up fresh every week and keep stoppered when not in use.
Sodium hydroxide solution, 1M:	Dissolve 40 gm of reagent grade sodium hydroxide in distilled water and dilute to 1000 ml.
Sodium acetate solution (iron-free), 10%:	Dissolve 10 gm of reagent grade sodium acetate in distilled water and transfer the solution to a 125 or 250 ml separatory funnel. Adjust the pH to 3.5-4.0, add 5 ml of the bathophenanthroline solution and mix thoroughly. Add 10 ml of isoamyl alcohol and shake the mixture for about 30 seconds. Drain off the aqueous layer into a second separatory funnel and repeat the extraction until the organic layer is colourless. Give the iron-free aqueous layer an extra wash with isoamyl alcohol to remove any remaining bathophenanthroline reagent and dilute the aqueous fraction to 250 ml with distilled water.
Isoamyl alcohol (Mallinckrodt, reagent grade):	
Ethyl acetate (Merck, reagent grade):	

Bromine water:	A saturated solution of bromine in distilled water.
Hydrochloric acid (reagent grade, iron-free) concentrated:	Pass the concentrated hydrochloric acid through a glass column containing ion-exchange resin IRA-400 (Rohm and Haas). Discard the first 3 bed-volumes.
Hydrochloric acid (iron-free), 6.5N:	Dilute 560 ml of iron-free concentrated hydrochloric acid to 1000 ml with distilled water.
Standard iron solution:	Dissolve an appropriate quantity of iron wire (99+% purity) in hydrochloric acid and dilute to the desired volume with distilled water. A suggested titer of this solution is: 1 ml of solution ≑ 2.0 micrograms of iron.

PROCEDURE

A. Initial Treatment

1. *Solid Samples*

Weigh out a suitable portion (Table 1) of the sample into a balance pan and transfer the sample to a 250-ml beaker. Add 10 ml of concentrated hydrochloric acid and 20 ml of distilled water. Cover and boil for 20 minutes. Cool, remove the watch glass and rinse down the sides of the beaker. Add 5 ml of concentrated nitric acid and 10 ml of 1:1 sulphuric acid. Evaporate the sample to dryness on the hot plate. If the sample is difficultly soluble, add a few drops of 40% hydrofluoric acid at the same time as the nitric and sulphuric acids. In such a case take the sample to sulphuric fumes twice and finally to dryness with sulphuric acid.

Digest the residue with about 5 ml of concentrated hydrochloric acid, dilute to 100 ml with distilled water and heat just under boiling for 10 minutes or until all soluble salts are in solution. Make the solution up to volume in an appropriate volumetric flask (Table 1). If the sample appears to be incompletely dissolved by this treatment carry out a sodium peroxide bomb fusion (7), only neutralize the leached melt with hydrochloric acid instead of nitric acid.

2. *Solution Samples*

Pipette an aliquot of the sample into a 125-ml Erlenmeyer flask, and dilute to about 25 ml. Add 2-3 ml of bromine water and boil off the excess bromine. If a precipitate forms, add a few drops of hydrochloric acid. Cool. Filter, if necessary into a beaker if no further dilution is required. If the iron content is high, filter into a volumetric flask of suitable size (Table 2), and aliquot a portion for the ethyl acetate extraction.

If a preliminary removal of contaminants is required, transfer an appropriate aliquot (Tables 1 and 2) of the sample to a 125- or 250-ml separatory funnel and add concentrated hydrochloric acid until the acidity of the solution is about 6.5 normal. The volume of the sample solution at this point should be about 50 ml. Cool and add 35-40 ml of ethyl acetate. Place a polyethylene stopper in the neck of the separatory funnel and shake the mixture for about 60 seconds. Allow the layers to separate (some hydrolysis of the ethyl acetate will take place) and drain off and discard the aqueous layer. Rinse the stem of the funnel with water. Wash the organic layer with 10 ml of 6.5 N hydrochloric acid solution by shaking the mixture for about 30 seconds and discarding the aqueous layer.

Strip the iron from the organic layer by adding about 15 ml of distilled water and shaking the mixture for 20-30 seconds. Drain off the aqueous layer into an appropriate volumetric flask (Tables 1 and 2) and wash the organic layer twice more with 5- to 10-ml portions of water from a wash bottle. Combine the washings, adjust the pH to the required range before diluting to volume and make up the solution to volume with distilled water. Aliquot the solution according to the procedure to be used for final iron determination (Tables 1 and 2).

B. Bathophenanthroline Colorimetric Finish

1. *Application Without Preliminary Separation of Contaminants*

Place an appropriate aliquot in a 50-ml beaker, add 5 ml of 10% hydroxylamine hydrochloride solution and 5 ml of 10% sodium acetate solution. Bring the solution to a boil for 1-2 minutes on a hot plate. Cool and adjust the pH to 3.5 to 4.0 by means of a pH meter. Place the sample solution in a 60-ml separatory funnel, measuring the volume of liquid present. (Because isoamyl alcohol and water are soluble in each other to some degree, the total volume should be carefully controlled.) Adjust the aqueous volume to the same level for samples and standards, which are carried along at the same time as the samples. Add by pipette 5 ml of 0.001 M bathophenanthroline reagent and mix. Then add by pipette 10 ml of isoamyl alcohol and stopper the funnel, using a glass stopper. Shake the mixture for about 60 seconds and allow the layers to settle. Drain off and discard the aqueous layer and transfer the organic layer to a centrifuge tube. After centrifuging the sample for about 30 seconds, read the absorbance on a Beckman "B" spectrophotometer using a 1-cm cell and a wave length of 535 mμ.

Correct the absorbance reading so obtained by subtracting the absorbance of a blank determination carried through the procedure. Determine the amount of iron corresponding to the corrected absorbance reading by means of a previously prepared calibration graph in which μ gm Fe per 10 ml of isoamyl alcohol has been plotted as ordinate against absorbance as abscissa. Verify recovery by carrying standards through the determination with the samples. Record the corrected value for the iron content of the extract.

2. *Application Following Ethyl Acetate Extraction*

Place an appropriate aliquot in a 50-ml beaker, add hydroxylamine hydrochloride and sodium acetate, and follow the procedure as in Section A, "Initial Treatment" omitting the pH adjustment step if the pH of the solution has been adjusted following the ethyl acetate extraction.

Table 1

Suggested Dilutions for Solids

Range %	Take gm	For extraction		Bathophenanthroline finish		Iron present in final aliq. μ grams Fe
		Dil. to ml	Take aliq. ml	Dil. to ml	Take aliq. ml	
<0.001	5	–	–	100	20	<10
<0.001	5	100	50	50	20	<10
0.001 – 0.005	2	–	–	100	20	4 – 20
0.001 – 0.005	2	100	50	50	20	4 – 20
0.005 – 0.020	2	–	–	100	5	5 – 20
0.005 – 0.020	2	100	25	100	20	5 – 20
0.020 – 0.10	1	–	–	100	2	4 – 20
0.020 – 0.10	1	100	20	100	10	4 – 20

Table 2

Suggested Dilution for Solutions

Range gm/l	Take ml	Ethyl acetate extraction	Dil. to ml	Take aliq. ml	Iron present in final aliquot μ grams Fe
<0.001	20	—	—	—	<20
<0.001	50	√	50	20	<20
0.001 – 0.005	4	—	—	—	5 – 20
0.001 – 0.005	20	√	100	20	4 – 20
0.005 – 0.020	10	—	100	10	5 – 20
0.005 – 0.020	25	√	250	10	5 – 20
0.020 – 0.10	2	—	100	10	4 – 20
0.020 – 0.10	2	√	100	10	4 – 20

CALCULATIONS

$$\% \text{ Fe} = \frac{\mu \text{ gm Fe, from graph (corr.)}}{10^6} \times \frac{\text{1st dilution}}{\text{aliquot taken}} \times \frac{\text{2nd dilution}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt., gm}}$$

If the absorbance reading is very low, report the iron content as "less than" the lower limit of detection. The limit of detection may be taken as 0.5 μ gm Fe in the final 10-ml isoamyl alcohol extract and the value to report may be calculated on this basis.

References

1. Method Fe-1.
2. Swank, H. W. and Mellon, M. G.: *Ind. Eng. Chem.*, Anal. ed., **9**, 406-9, 1937.
3. Method Fe-3.
4. Smith, G. Frederick, McCurty, W. H., Jr., and Diehl, Harvey: *Analyst*, **77**, 418-22, 1952.
5. Guest, R. J., and Roloson, F. P.: Radioactivity Division, *Mines Br., Ottawa.* Topical Report No. TR-137/57, Dec. 10, 1956.
6. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I.: Applied Inorganic Analysis, pp. 134-7, New York, John Wiley and Sons, 1953.
7. Ingles, J. C.: Radioactivity Division, *Mines Br., Ottawa*, Topical Report No. TR-131/55, Aug. 22, 1955. (see Method U-1)

The Determination of Mercury: Distillation-Titration Method

METHOD Hg-1

SCOPE

The procedures given below may be used to determine mercury in ores, solids and sulphide precipitates. This includes ores containing sulphur, organic matter, oxides of arsenic and antimony, and sulphides. Its principal application has been to products from electrolytic and amalgam reduction processes for uranium recovery.

RANGE

From 5 to 500 mg of mercury may be determined in samples weighing up to 2 gm, with a maximum error of 0.3 to 1.0 mg, depending on the mercury content.

OUTLINE

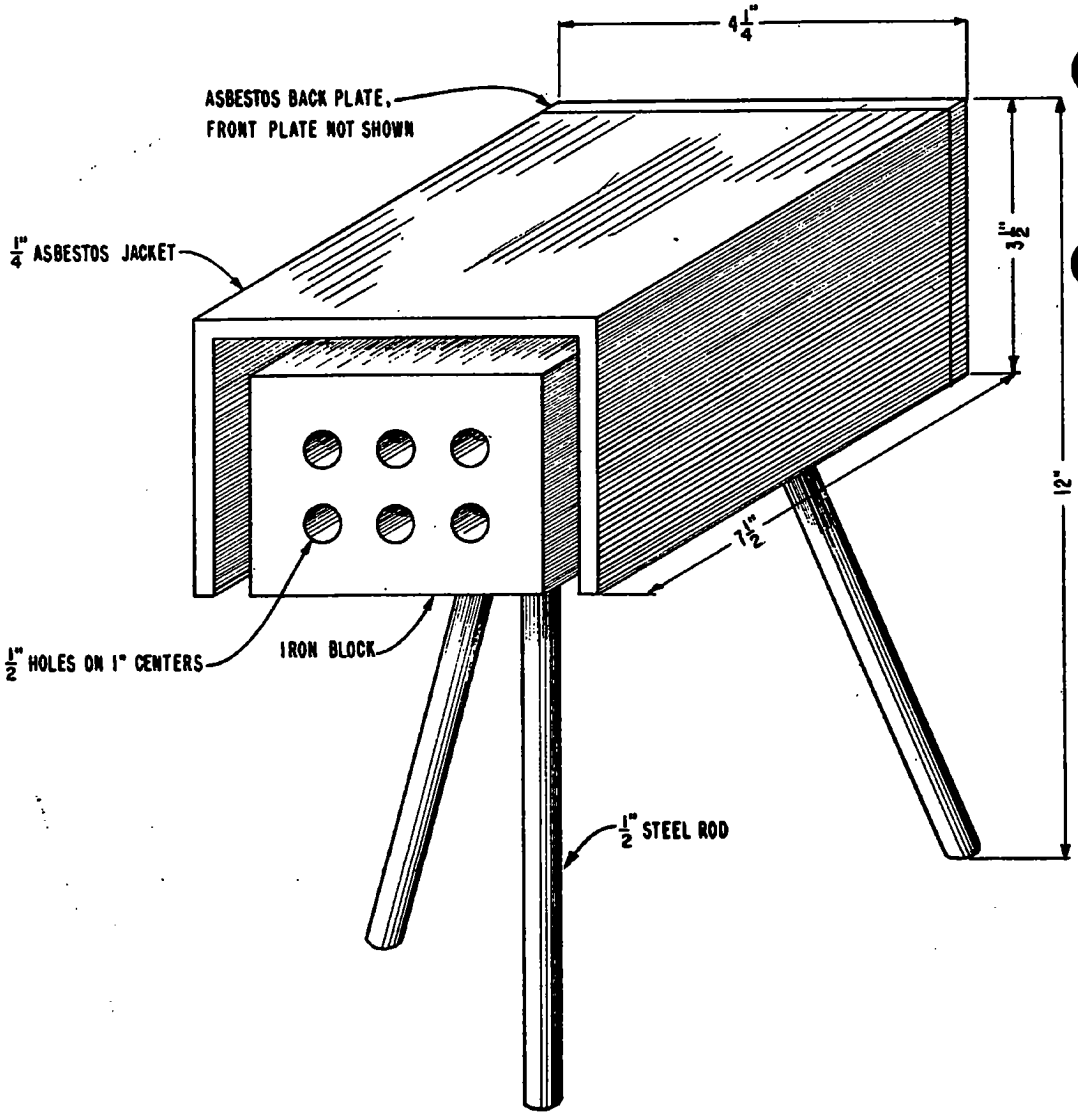
The powdered ore is mixed with lime, and heated at 500°C in a glass tube which is closed at one end. The mercury condenses in the cool end of the tube. It is then dissolved in hot nitric acid and the solution is titrated with thiocyanate, using ferric nitrate or sulphate as an indicator.

APPARATUS

Special furnace:	*See diagram, page 2* (other means of heating may be used).
Distillation tubes, Pyrex:	10 mm OD by about 30 cm long. One end of the tube is sealed by drawing to a conical tip. The other or open end is fire-polished.
Brass or copper plugs:	to fit the glass tubes. These plugs are made of gauze or "scouring pads"; gauze is the more reliable.

REAGENTS

Sand or crushed granite, −10 + 20 mesh:	
Powdered lime, freshly calcined:	
Potassium thiocyanate solutions N/10 and N/100:	These may be standardized against silver nitrate or against standard mercury.
Hydrogen peroxide 10-volume (3%):	in a dropping bottle.
Ferric nitrate:	10 gm in 100 ml of water. This must be free from halides.
Potassium permanganate, 2%:	in a dropping bottle.



MERCURY DISTILLATION FURNACE

Potassium chlorate:	crystals.
Potassium chlorate:	powder.
Cupric oxide:	powdered.
Iron filings:	clean and free from grease or oil.

PROCEDURE

A. *For Ores Containing Little Sulphide, Free Sulphur or Organic Matter*

Clamp the distillation tube vertically with the open end up. Add enough sand or crushed granite to fill the conical end of the tube. Add a thin layer of lime. Mix the sample in an evaporating dish with about half its weight of lime

and add the mixture to the tube through a short-stemmed funnel. If there is much mercury in the sample, clean the dish and funnel with a little more lime and add this to the tube. Brush the dish and funnel with a camel-hair brush. Add a final 1-cm layer of lime and a 1-cm layer of sand. Finally push the gauze plug into place against the top of the charge.

Hold the tube horizontally and tap it on the bench top to open a channel about the ore for escaping vapors. Place the tube in the furnace with the empty part of the tube projecting and shielded from the heat. The temperature of the furnace should be between 350°C and 550°C. Heat for 15 minutes. Let cool.

Pour 5 ml of hot concentrated nitric acid into a test tube. *Put on a pair of safety goggles or a face mask.* Withdraw the tube from the furnace cautiously. Place the tube, open end down, in the test tube. Discard the tube if the gauze plug slips down.

Break the bead from the closed end of the tube and with a pipetting bulb draw the acid up into the tube nearly to the brass plug. Remove the bulb and let the acid drain from the tube. Repeat to recover all the mercury. When the mercury is completely dissolved transfer the solution to a 100-ml beaker. Add 5 ml of water to the test tube and rinse the distillation tube by drawing the water up into the distillation tube. Add the wash water to the solution in the beaker and repeat the washing once or twice.

Adjust the volume to about 30 ml, and add permanganate solution dropwise until a permanent pink colour is produced. Cool the solution and bleach the excess permanganate with one or two drops of hydrogen peroxide. Add about 2 ml of the ferric nitrate solution and titrate with standard potassium thiocyanate. If less than 50 mg of mercury is present use N/100 thiocyanate. If more than 50 mg of mercury is present use N/10 thiocyanate.

B. *For Samples Containing Elemental Sulphur, Pyrite and Oxides of Arsenic or Antimony*

These contaminants may distill with the mercury and combine with the distillate. Such contamination is indicated by discoloration of the mercury and by a black residue remaining undissolved by the nitric acid.

Mix the sample with a mixture of cupric oxide and lime and proceed as above.

When the sample contains 20% sulphur the ratio of cupric oxide to lime is 2 to 1. When the sample contains less sulphur the ratio of cupric oxide is reduced.

C. *For Samples Containing Organic Matter and Sources of Free Sulphur*

Organic matter may discolour the solution and mask the end-point. If it is present, mix potassium chlorate crystals to the sand first added to the tube. The potassium chlorate should not exceed 10% of the weight of the sand. Mix the sample with 1 to 2 gm of cupric oxide and 0.1 to 0.3 gm of potassium chlorate powder. To the lime which follows the sample add an equal part of cupric oxide and charge the tube as above.

Insert the tube into the rear of the furnace so that only the cupric oxide-lime layer and the sand layer are being heated. After 2 or 3 minutes, start moving the tube forward 0.5 to 1 cm at a time to avoid sudden evolution of gas. When the tube has reached its usual position heat for 5 minutes longer and proceed as usual.

D. *For Filtered Hydrogen Sulphide Precipitate*

Precipitate the mercury with hydrogen sulphide, using cupric sulphate as a carrier. Filter. Dry the precipitate at a low temperature.

If the precipitate has been filtered on paper proceed as in Section C. Any part of the filter paper entirely free from precipitate should be rejected.

E. *Troublesome Ores Containing Organic Material*

These may be leached by a Kjeldahl digestion using nitric and sulphuric acids.

CALCULATION

1 ml N/10 KCNS = 0.01003 gm mercury

1 ml N/100 KCNS = 0.001003 gm mercury

$$\% \text{ Hg} = \frac{\text{Titration (ml)} \times \text{factor} \times 100}{\text{sample weight}}$$

If no titration is obtained, the result should be reported as "less than" the minimum amount detectable, rather than using the term "not detectable". The minimum amount detectable with the N/100 KCNS solution may be taken as 0.00005 gm and the value to report would be given as:

$$\% \text{ Hg} = \frac{\text{less than } 0.00005 \times 100}{\text{sample wt.}}$$

Reference

1. Bouton, C. M., and Duschak, L. H.: *U. S. Bureau of Mines*, Technical Paper 227, 1920.

The Infra-Red Absorptiometric Determination of Kerosene and other Aliphatic Solvents in Raffinates

METHOD Ke-1

SCOPE

This method is intended to provide a rapid reproducible estimate of solvent losses to raffinates in solvent extraction systems using aliphatic diluents such as kerosene to carry the active solvent.

RANGE

The infra-red absorptiometric finish will cover the range 0.0005 ml to 0.05 ml of kerosene in the 10-ml carbon tetrachloride solution. Assuming a 500-ml sample of raffinate can be extracted, this will give a lower limit of 1 ppm kerosene.

OUTLINE

The sample is collected directly from the discharge line of the solvent extraction plant in the container used for extraction of the kerosene so that separation cannot occur. The kerosene is then extracted with small portions of carbon tetrachloride and the successive carbon tetrachloride fractions (dried to prevent damage to the rock salt cell windows of the infra-red spectrometer) are combined and made to volume. The carbon tetrachloride solution containing all the kerosene from the sample is then submitted for the infra-red determination. This is based on optical density measurements of the extract at the CH_3, CH_2, and CH stretching frequencies in the region of 3.4 microns.

APPARATUS

Bottles, reagent, narrow mouth, with ℈ stopper:	1000 ml size.
Pipette:	5 ml size.
Graduated cylinders:	5 ml and 500 ml sizes.
Mechanical shaker, reciprocating type:	e.g. A. H. Thomas Cat. No. 8915.
Beakers, Pyrex Griffin:	10 ml size.
Flasks, volumetric:	10 ml size.

REAGENTS

Carbon tetrachloride, C.P.:

Cupric sulphate, anhydrous:

PROCEDURE

Collect a sample of suitable size (100-600 ml) in a tared 1-litre ₮ glass-stoppered bottle. Weigh the bottle to determine the sample size. Add 3 ml of carbon tetrachloride and shake vigorously for about 15 minutes on a mechanical shaker. Remove, let settle, and withdraw the carbon tetrachloride layer as completely as possible using a 5-ml pipette. Transfer it to a 10-ml beaker containing 0.5 grams of anhydrous cupric sulphate, then decant it into a 10-ml volumetric flask. Repeat the extraction process twice more, drying each carbon tetrachloride extract with a fresh portion of anhydrous cupric sulphate in a separate 10-ml beaker, then decanting into the beaker used for the previous extract and finally into the volumetric flask. Rinse all the beakers successively using one 2-ml portion of carbon tetrachloride. Transfer this to the volumetric flask and make to volume (the loss of carbon tetrachloride by vaporization is fairly high). Finally, measure the volume of the aqueous layer using a graduated cylinder or measure its specific gravity roughly and calculate the volume taken from the weight.

At the same time take a suitable portion of carbon tetrachloride for use as a blank and for the preparation of standards. Suitable standards are prepared by diluting 0.1 ml of kerosene to 50 ml and re-diluting 1-, 2- and 5-ml portions of this solution to 10 ml with carbon tetrachloride. Submit the suitably labelled samples and standards to the infra-red laboratory for quantitative determination of kerosene, ml per 10 ml carbon tetrachloride.

Details of the infra-red procedure will be found in reference (1).

CALCULATIONS

$$\text{Kerosene, ppm} = \frac{\text{ml kerosene per 10-ml extract}}{\text{volume of solution taken, ml}} \times 1000$$

Reference

1. Simard, R. G., Hasegawa, I., Bandaruk, W., and Headington, C. E.: *Anal. Chem.*, **10**, 1384, 1951.

Oven and Moisture-Meter Methods for Determining Moisture in Ore Pulps and Products, Percentage Loss in Weight Determination

METHOD M-1

SCOPE

This method is intended for the determination of moisture in ores and products that do not undergo decomposition or oxidation at a temperature of 105°C. Since this is not always known, the results should preferably be reported as "% loss in weight".

RANGE

The lower limit for loss in weight is 0.05% for the oven method and 0.2% for the "Moisture-Meter". These quantities also indicate approximately the accuracy with which the weight loss can be determined.

OUTLINE

The oven moisture method determines all constituents of the sample volatile at 105°C. The principal constituent volatile at this temperature is water. With some materials, for example ammonium diuranate, other constituents volatilize slowly at this temperature, and more rapidly as the temperature is raised

$$9\ (NH_4)_2\ U_2O_7 \longrightarrow 2\ N_2 + 14\ NH_3 + 15\ H_2O + U_3O_8 \quad (1)$$

For this reason, the temperature must be carefully maintained and the actual temperature at the shelf where the samples are placed should be checked. A portable recording thermometer (e.g. Tag Fahrenheit D 217399 80-220°F—Weston Electric Instrument Corp., Newark 5, N.J.) is convenient for this purpose.

Some materials, such as uranous phosphate precipitate and pyritic ores tend to oxidize and thus gain weight. The moisture content of such material should be determined using weighings at frequent intervals, or a fixed time interval used which has been shown experimentally to give reproducible values.

It is usually found that ores will have lost 90% of their moisture content in 4 hours, and 95% in 24 hours, at 105°C. A drying period of 48 hours is considered ample.

An alternative rapid procedure is also presented, using a combination balance and infra-red heating device called the "Cenco Moisture Meter". Similar devices are available and may be used in the same way. These heat the sample very rapidly. The temperature rises quickly to 100°C and stays there as long as water is being volatilized. When the water is gone, the temperature again rises, and has been observed to yield a temperature of 245°C in 15

minutes (using a 250 watt IR bulb). At this extreme temperature, the effects of decomposition and oxidation are accelerated and errors of several percent in the reported moisture value can occur. It is believed that this is largely avoided by noting the moisture value at regular intervals and taking the highest value obtained in the first few minutes, ignoring subsequent slow changes up or down. Ores containing 10-15% of moisture reach this value in 2 minutes with the 250 watt bulb and a time of 10 minutes should never be exceeded.

APPARATUS

Oven:	Capable of holding 20 moisture dishes and of maintaining a temperature of 105 ± 5° C on shelves where the dishes will be placed. It must also be suitably vented to provide mild circulation of air over the samples.
Dishes, weighing:	Low form, with ground glass stoppers.
Desiccator:	
Desiccant:	
Balance:	Accurate to 1 mg.
"Cenco Moisture Meter":	Cat. No. 26675, Central Scientific Co., Chicago.
Disposable sample pans for above:	Cat. No. 26678.
Powerstat transformers:	Cat. No. 80297a.

PROCEDURE

A. *Oven Method*

Dry two wide-mouth weighing bottles (per sample) in the oven at 105°C for 24 hours with the lids off. Set the lids of the dishes on a slant so as not to close the dishes, and desiccate 30 minutes in a desiccator with fresh desiccant. Cover the cool dishes and weigh. Remove the lids, transfer approximately 5-gram portions of the sample to each dish with a minimum of delay, cover at once and reweigh. (Note: do not keep the cover off the sample bottle any longer than is absolutely necessary.) The difference in weight between the empty dish and the weight of the dish with the sample is the "original weight of sample". The lids are then removed carefully so as not to cause any loss of sample, and dishes and lids are placed in the oven at 105°C for 24 hours. (Temperature should be checked with thermometers on the shelves above and below the one on which the dishes are placed.) Remove, desiccate the open dish and lid (otherwise, on cooling, the lid may be hard to remove) then cover and weigh. Remove the lid and place the dish and lid in the oven as before for a further 24-hour period. Continue this procedure until no further loss in weight is noted. The final weight of dish plus dry sample, subtracted from the original weight of dish plus sample as received, is the "loss in weight".

B. *Moisture-Meter Method*

See Figures 1, 2, and 3 for the letter designations of the parts of the instrument. Set up the instrument as described in the instructions.

For use, raise the lamp housing (m) by means of the handle (n) located directly below the viewing window. This gives access to the sample pan holder.

Place an empty disposable pan on the pan holder (a), set the moisture scale (f) at 100%, against the index mark (g) using the knurled wheel (e) on the right-hand side of the instrument. Tighten the zero adjusting knob (k) (on the left-hand side) by turning it clockwise, and raise or lower it to bring the pointer (h) to the index mark (g). If the zero adjusting knob is moved downward to its

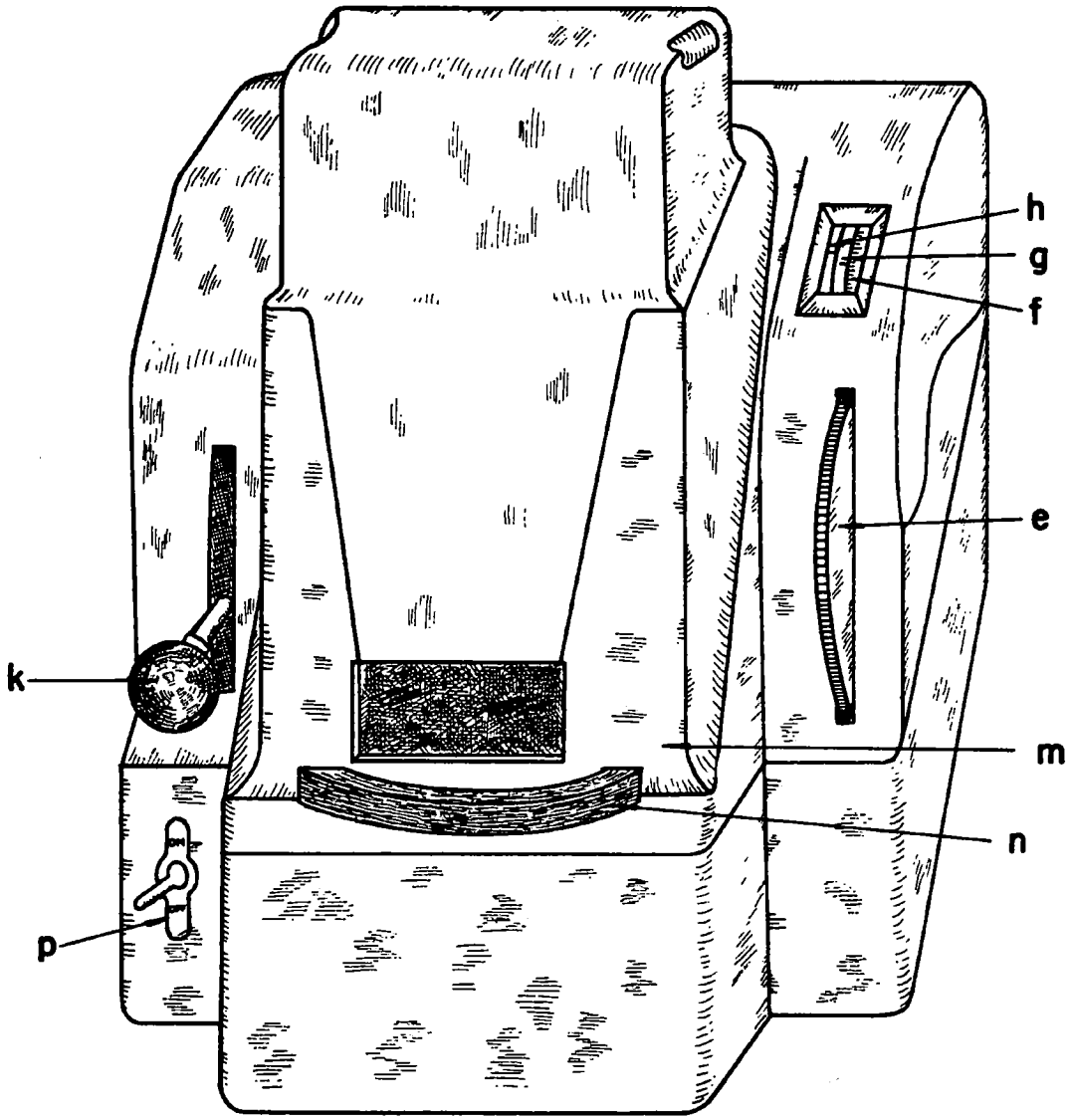


Figure 1

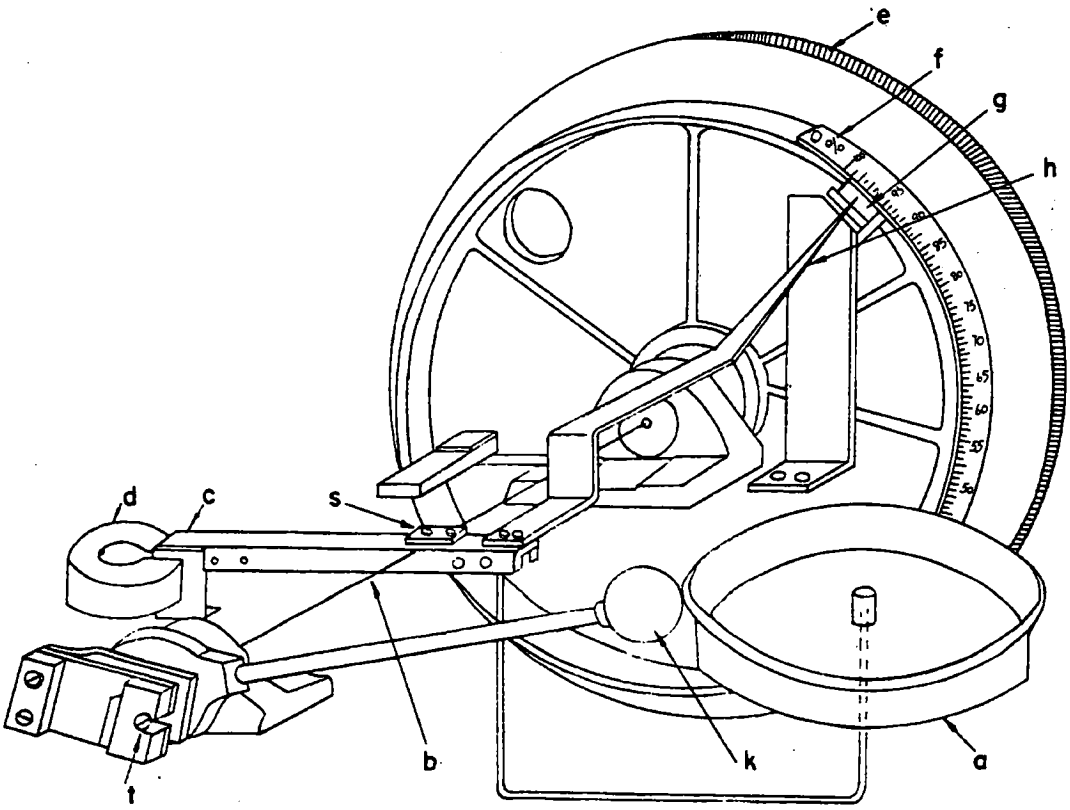
CENCO MOISTURE BALANCE

lowest position and the pointer remains above the line on the index, loosen the knob by turning it one revolution counterclockwise. Raise the loosened knob as high as possible, tighten, and by lowering bring the pointer in line with the index. Repeat the procedure if necessary. Similarly, if with the adjusting

knob in its uppermost position the pointer remains below the index line, loosen the knob and move the arm down to its lowest position. Then tighten and raise it to bring the pointer in line with the index.

Finally, loosen the knob and lower it to prevent the balance being put out of adjustment. When pointer, index and scale are lined up as in Figure 3 (A), the balance is ready to use.

Now rotate the knurled wheel (e) until the 0% line of scale (f) is aligned with the index (g). The pointer will move above the index. Carefully distribute the material on the pan, adding just sufficient material to bring the pointer in



a Sample pan
b Torsion wire
c Counter weight
d Magnet
e Knurled wheel
f Graduated Scale
g Index
h Pointer
k Zero Adjusting Knob
s Clamping screws
t Tension Release Screws

Figure 2

NO. 26675 CENCO MOISTURE BALANCE INTERNAL MECHANISM

line with the index as in Figure 3 (B). About 5 grams of sample is required; but the exact amount need not be known since it has been taken into account in the construction of the scale.

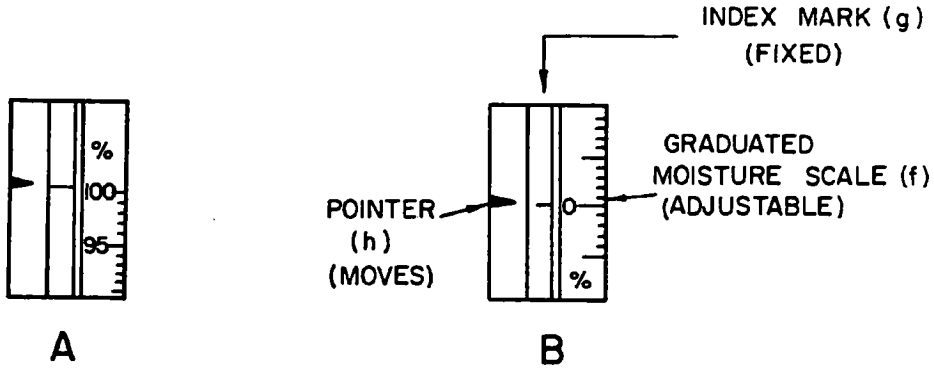


Figure 3

MOISTURE SCALE, INDEX AND POINTER OF MOISTURE METER

With the correct amount of sample on the pan, lower the lamp housing and turn on the switch (p). The sample will begin losing moisture and the pointer will move upward. Bring the pointer back in line with the index by turning the knurled wheel. The reading on the scale opposite the index represents the moisture lost up to that moment, if the pointer is in line. Continue the procedure until the pointer stops moving and no further change in its position occurs for several minutes. (Further small changes after a steady result has been obtained indicate decomposition or oxidation.) The reading of the scale opposite the index line is the percentage moisture content of the sample and no calculation is needed.

If there is too rapid heating of the sample the lamp can be plugged into a Powerstat and the voltage reduced, or a less powerful bulb can be used.

CALCULATION

A. *Oven Method*

$$\% \text{ Loss in Weight (105°C)} = \frac{\text{loss in weight}}{\text{original weight of sample}} \times 100$$

B. *Moisture-Meter Method*

% Loss in Weight = as read from the dial (f) of the instrument.

References

1. Mellor, J. W.: A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. XII pp. 65-9, London, Longmans Green and Co. Ltd., 1947.
2. Directions for Cat. No. 26675, Cenco Moisture Balance, Chicago, Central Scientific Co., undated.

The Gravimetric Determination of Magnesium as Pyrophosphate

METHOD Mg-1

SCOPE

The method is applicable to all ores and mill products containing magnesium in sufficient quantities to be determined gravimetrically (5).

RANGE

The range covered is from 0.0005 to 0.2 gm. Larger amounts can be determined, but these larger precipitates are harder to ignite.

OUTLINE

Magnesium is precipitated from an ammoniacal solution as magnesium phosphate. The precipitate is ignited and weighed as magnesium pyrophosphate. Ordinarily magnesium is determined on the filtrate from the calcium oxalate precipitation as outlined under METHOD Ca-1. Interfering elements such as barium, or any calcium or strontium which may have escaped precipitation as the oxalates, are separated by precipitating them as sulphates. Since many other elements also form insoluble phosphates, the precipitation of magnesium is usually made after the removal of these interfering elements by hydrogen sulphide, ammonium hydroxide, ammonium sulphide and ammonium oxalate separations.

APPARATUS

Gas burner, Meker:	
Hot plate:	
Balance, analytical:	
Crucibles, platinum:	25 or 30 ml size.
Tripod:	
Triangles:	silica-covered.
Crucible tongs, platinum tipped:	
Beakers, Griffin:	250, 400, 600, 800 ml sizes.
Beakers, Berzelius:	300, 400 ml sizes.
Beaker covers:	Speedyvap.
Beaker covers, watch glass form:	
Beaker tongs:	
Filter paper:	Whatman No. 41H, No. 30 and No. 42.

Funnels, Bunsen long stem: 65 and 75 mm size.

Pipettes, volumetric: 5, 10, 25 and 50 ml size.

Bottles, washing: 1 litre size.

Bottles, reagent:

Bottles, dropping:

Crucibles, fritted glass: medium porosity.

Flasks, filtering, with side tube: 500 ml size.

Crucibles, alundum:

Desiccator:

REAGENTS

Sodium carbonate:

Potassium nitrate:

Oxalic acid:

Ammonium oxalate:

Nitric acid:

Sulphuric acid:

Hydrochloric acid:

Perchloric acid:

Hydrogen sulphide: Cylinder or lecture bottle.

Ammonium hydroxide:

Sodium sulphite:

Ammonium chloride:

Sodium hydroxide:

Hydrogen peroxide:

Calcium carbonate:

Silica, pure, fine:

Methyl red indicator solution: Dissolve 0.02 gm of the indicator in 100 ml of hot water, let the solution cool, and filter.

Ammonium sulphide solution: Saturate 10% ammonium hydroxide solution (1:9, v/v), with hydrogen sulphide.

Ammonium sulphide wash solution: Add 10 ml of ammonium sulphide solution to 1 litre of water containing 10 gm of ammonium chloride and a few drops of ammonium hydroxide.

Standard calcium solution: Dissolve 1.79 gm of calcium carbonate in as little hydrochloric acid as possible and dilute to 1 litre. 1 ml = 1 mg CaO.

Tartaric acid:

Diammonium phosphate:

Ethyl alcohol:

Methyl alcohol:

Citric acid:

Hydrobromic acid:

Bromine:

Bromine water: A saturated solution of bromine in distilled water.

PROCEDURE

A. General Method

1. *Preliminary Treatment*

(a) *Ores, Precipitates and Other Solid Samples—Acid Decomposition and Carbonate Separation*—Weigh a portion of the sample, preferably containing 0.005 to 0.2 gm of magnesium, into a 250-ml beaker. Add 20 ml of hydrochloric acid, 20 ml of water and 5-10 ml of hydrobromic acid. Heat to boiling and boil for 20-30 minutes. If the arsenic or antimony contents are high, repeat the hydrochloric-hydrobromic treatment. Cautiously add 5-10 ml of nitric acid and boil until the excess bromine is expelled. Add 8-10 ml of perchloric acid. If the sample is high in fluorides and low in silica, add a few milligrams of fine pure silica. Evaporate to dense fumes, cover the beaker and reflux for 15-20 minutes. Cool, wash down the sides of the beaker with distilled water, dilute to 30-40 ml and digest until the soluble salts are in solution. Filter through a No. 30 Whatman filter paper and wash the paper and residue thoroughly with distilled water. Reserve the filtrate. If the fluoride content was negligible or if the silica content was high, dehydration of the silica can be accomplished by evaporating the solution to dryness with hydrochloric acid instead of refluxing with perchloric acid. Transfer the paper and residue to a platinum crucible, dry, char, and ignite the filter paper. Fuse the residue with about six to seven times its weight of sodium carbonate.

If phosphates are present only in negligible amounts, or if elements such as iron, aluminum, and titanium greatly exceed the phosphate content, omit the subsequent sodium hydroxide-sodium carbonate separation. Dissolve the melt directly in hydrochloric acid and take to dryness to dehydrate silica. Digest the residue with water, filter and combine the filtrate with the main body of the solution. Dilute the combined filtrates to 200-250 ml.

If phosphates are present and the iron or titanium content is low, transfer the cooled melt to the original beaker, add 50-60 ml of water and digest on the hot plate until the mass is thoroughly disintegrated. Filter through a No. 30 Whatman filter paper and wash the paper and residue with a hot 5 percent solution of sodium carbonate. Discard the filtrate and washings. Place the beaker containing the reserve filtrate under the funnel and dissolve the residue from the paper with a little hot 1:1 hydrochloric acid. Wash the paper with hot water. If necessary, fuse the residue again with sodium carbonate and repeat the water extraction. Dilute the combined filtrates to 100-150 ml.

(b) *Solid Samples, Fusion Decomposition (Arsenides, Sulphides and Easily Reducible Metals Absent, Phosphate Present)*—Weigh a portion of the sample, preferably containing 0.005 to 0.2 gm of magnesium, into a platinum crucible. Add about six to eight times as much sodium carbonate as sample, mix thoroughly, and cover with a little sodium carbonate and 0.5 gm of potassium nitrate. Fuse to a clear melt, cool, and digest the melt in 200-250 ml of water until the mass is thoroughly disintegrated. Filter through a No. 30 Whatman filter paper and wash the paper and precipitate with a hot 5 percent solution of sodium carbonate. Discard the filtrate. Dissolve the precipitate in hydrochloric acid. If an insoluble residue remains, filter it off and fuse it with sodium carbonate. Digest the melt in water, filter and wash as before. Dissolve the precipitate in hydrochloric acid and combine the acid solutions. Dilute the combined filtrates to 100-150 ml.

(c) *Solid Samples, Fusion Decomposition (Phosphate Low, or Iron, Aluminum and Titanium High)*—If the content of such elements as iron, aluminum, and titanium greatly exceeds the phosphate content, carry out a carbonate fusion as in subsection (b), but omit extraction of the sodium carbonate melt. In this case dissolve the melt in hydrochloric acid and evaporate to dryness to dehydrate the silica. Digest the residue with water, filter, dilute the filtrate to 100-150 ml.

(d) *Solutions*—Pipette an aliquot portion of the sample into a 250-ml beaker. Add 5-10 ml of nitric acid and evaporate to dryness. If organic material is present, repeat the nitric acid treatment. Digest the residue with 20-30 ml of water and 4-5 ml of hydrochloric acid. Filter if necessary, dilute to 100-150 ml and carry out the sodium hydroxide-sodium carbonate, hydrogen sulphide, ammonium hydroxide, ammonium sulphide and oxalate separations as outlined below; *or* the rapid ammonium oxalate procedure as outlined in Section B, page 6.

2. *Carbonate – Hydroxide Separations, (to be included only if the phosphate content is high, and the iron and titanium content is low)*

Nearly neutralize the solution with sodium hydroxide. Add 3-4 gm of sodium carbonate and 3-4 ml of 3 percent hydrogen peroxide. Digest on the hot plate for 15-20 minutes to coagulate the precipitate, cool, let settle and filter through a No. 30 Whatman filter paper. Wash the paper and residue with a hot 5 percent sodium carbonate solution. Discard the filtrate and washings. Wash most of the precipitate back into the beaker, place the beaker under the funnel and dissolve any precipitate remaining on the paper with hot 1:1 hydrochloric acid. Wash the paper with hot water. Dissolve any undissolved precipitate in the beaker with a little hydrochloric acid and add 4-5 ml in excess.

If the phosphate content is low and the iron and titanium content is high, omit the carbonate-hydroxide separation. Nearly neutralize the solution with ammonium hydroxide, acidify with hydrochloric acid and then add 4-5 ml hydrochloric acid in excess.

3. *Hydrogen Sulphide Separation*

Dilute the solution to 100-150 ml, add 0.5 to 1 gm of sodium sulphite, heat to boiling and boil until the excess sulphur dioxide is expelled. Pass hydrogen sulphide through the solution for 15-20 minutes. Cool, filter through a No. 42 Whatman filter paper into a 400-ml beaker and wash the paper and precipitate with an acidulated hydrogen sulphide solution (10 ml of hydrochloric acid in 1 litre of water saturated with hydrogen sulphide). Do not let the paper or precipitate become dry during filtration or washing. Reserve the precipitate for the determination of copper, if required.

4. *Ammonium Hydroxide Separation*

Heat the filtrate to boiling and boil until the excess hydrogen sulphide is expelled. Add 2-3 ml of bromine water, and enough ferric chloride to combine with any phosphates present. Boil until the excess bromine is expelled, dilute to 200 ml, add 2 gm of ammonium chloride and a few drops of methyl red indicator solution. Neutralize the solution with 1:1 ammonium hydroxide plus 1 ml excess and boil for 3-4 minutes. Filter through a No. 41H Whatman filter paper, and wash the paper and precipitate with a hot 2 percent solution of ammonium chloride. Reserve the filtrate. Dissolve the precipitate in hot 1:1 hydrochloric acid, dilute to 150-200 ml, add 2 gm of ammonium chloride, and a few drops of methyl red indicator. Reprecipitate the iron and titanium, filter and wash as before. Combine the filtrates and discard the precipitate.

5. *Ammonium Sulphide Separation*

If such elements as manganese, nickel and cobalt are present, bubble hydrogen sulphide through the filtrate for 10-15 minutes and filter through a No. 42 Whatman filter paper into a clean beaker. Wash the paper and precipitate with the ammonium sulphide wash solution. Neutralize the filtrate from either the ammonium hydroxide or ammonium sulphide separation with hydrochloric acid and boil to expel any excess hydrogen sulphide. Add 5-6 ml of bromine water and evaporate to 150-200 ml. Filter, if necessary, into a clean 400-ml beaker and wash the paper and precipitate with a hot 1 percent hydrochloric acid solution. Discard the paper and residue.

6. *Ammonium Oxalate Separation*

Dilute the filtrate to 200-250 ml. If the magnesium content is high, add (by pipette) 10 ml of the standard calcium oxide solution, 2-3 drops of methyl red indicator and 15-20 ml of a saturated oxalic acid solution. If the magnesium content is low, omit the addition of the standard calcium oxide. Heat the solution to boiling and then slowly add 1:1 ammonium hydroxide, with stirring, until the solution is just alkaline (i.e. just turns yellow). Add 5 gm of ammonium oxalate and heat just below boiling for 20-30 minutes. Allow the solution to cool for 1 hour and filter through a No. 42 Whatman paper. Wash the precipitate a few times with a cool 0.1 percent solution of ammonium oxalate. Reserve the filtrate. Dissolve the washed oxalate precipitate in 15-20 ml of hot 1:1 hydrochloric acid, dilute to 150-200 ml, add 2-3 drops of methyl red, 5-10 ml of saturated oxalic acid solution, 1 gm of tartaric acid and heat just below boiling. Slowly add 1:1 ammonium hydroxide until the solution is just alkaline, add 3 gm of ammonium oxalate and digest on the hot plate for 15-20 minutes. Cool for 1 hour and filter through a No. 42 Whatman filter paper. Wash the paper three or four times with a cool 0.1 percent ammonium oxalate solution and then five to six times with hot water. Reserve the precipitate for the determination of calcium. Combine the filtrates and add 50 ml of nitric acid. Cover the beaker, heat gently until the evolution of gas ceases and then evaporate to a small volume. Cool, add additional nitric acid if the ammonia salt content is excessive, and then evaporate just to dryness. Cool, and wash down the sides of the beaker with distilled water. Add 10-15 ml of hydrochloric acid and evaporate just to dryness. Cool, add more hydrochloric and again evaporate to dryness. Digest the residue with 100-150 ml of water and 1 ml of hydrochloric acid until the soluble salts are in solution.

7. *Magnesium Precipitation*

Dilute to 250-300 ml with distilled water, cool, add enough diammonium phosphate (as crystals or a freshly prepared 10 percent solution) to provide at least a tenfold excess and preferably 1 gm in addition for each 100 ml of solution. While stirring vigorously, add ammonium hydroxide slowly until the solution is alkaline to litmus paper, then add 10 ml excess for every 100 ml of solution. Continue stirring for 5 minutes (do not scrape the sides of the beaker) and let stand for at least 4 hours. Filter through a No. 42 Whatman filter paper and wash ten to twelve times with a 5 percent solution of ammonium hydroxide. Discard the filtrate. Place the beaker under the funnel, dissolve the precipitate in warm dilute (1:4) hydrochloric acid and clean the sides of the beaker and stirring rod with the acid. If the amount of magnesium is low and the barium content is negligible, transfer the solution to a smaller beaker, dilute to 50-150 ml, add

0.1 to 0.3 gm of diammonium phosphate, and then add ammonium hydroxide drop by drop with constant stirring until the precipitate has formed and the solution is alkaline. Add 5 ml excess ammonium hydroxide for each 100 ml of solution, stir for 5 minutes and let stand for at least 4 hours. Filter through a clean No. 42 Whatman filter paper, clean the beaker and stirrer and wash the paper and precipitate with a cool 5 percent solution of ammonium hydroxide. Transfer the paper and precipitate to a weighed platinum or alundum crucible, char the paper slowly without allowing it to ignite, and burn off the carbon gradually. Finally ignite for 30 minutes at 1000 to 1050°C. Cool in a desiccator and weigh. If barium is present, transfer the hydrochloric acid solution of the first magnesium phosphate precipitate to a 250-ml beaker, add 2-3 ml of 1:1 sulphuric acid and evaporate to dense fumes of sulphur trioxide. Dilute to 100-150 ml and digest at 50-60°C for a few minutes. Add 10-15 ml of ethyl alcohol or a mixture of ethyl and methyl alcohol, let stand for 1 hour and filter through a No. 42 Whatman filter paper. Wash first with a hot 1 percent sulphuric acid solution and then with hot water. Discard the paper and precipitate. Heat the filtrate to boiling and boil to expel excess alcohol. Cool, add 1 ml of hydrochloric acid and 2-3 gm of diammonium phosphate. Add ammonium hydroxide drop by drop, with stirring, until the solution is neutral, then add 5 ml of ammonium hydroxide in excess for every 100 ml of solution. Filter through a No. 42 Whatman filter paper and wash the precipitate with a cool 5 percent ammonium hydroxide solution. Discard the filtrate. Dissolve the precipitate in warm dilute (1:4) hydrochloric acid and transfer the solution to a 250-ml beaker. Dilute to 50-100 ml with distilled water, add 0.1 to 0.3 gm of diammonium phosphate, neutralize with ammonium hydroxide, filter, wash, ignite, and weigh as before. Record the weight of the precipitate.

B. Rapid Method for Dolomitic Limestones and Brucite (Hydrogen Sulphide Group, Phosphates and Manganese Absent or Present in Negligible Quantities)

Weigh a portion of the sample, preferably containing 0.005 to 0.2 gm of magnesium, into a 250-ml beaker. Add 20 ml of hydrochloric acid and 5-10 ml of hydrobromic acid. Heat to boiling and boil for 15-20 minutes. Cool slightly and cautiously add 5 ml of nitric acid. Add 5 ml of perchloric acid, evaporate to fumes, cover the beaker and reflux for 15-20 minutes. Cool, wash down the sides of the beaker, dilute to 30-40 ml with distilled water and digest until the soluble salts are in solution. Filter through a No. 30 Whatman filter paper into a 400-ml beaker and wash the paper and residue with a hot 1 percent hydrochloric acid solution. Dilute the filtrate to 200 ml, add 4-5 gm of ammonium chloride and 10 ml of a 10 percent solution of citric or tartaric acid. Cool to 70-80° C, add 5 gm of ammonium oxalate and 3-4 drops of methyl red indicator. If the magnesium content is high, add (by pipette) 10 ml of the standard calcium oxide solution and then carefully add 1:1 ammonium hydroxide until the solution just turns yellow. Heat just below boiling for 15-20 minutes and filter through a No. 42 Whatman filter paper. Wash the precipitate three or four times with a 0.1 percent ammonium oxalate solution. Reserve the filtrate and washings. Wash most of the precipitate back into the precipitation beaker with distilled water. Place the beaker under the funnel. Dissolve any remaining precipitate from the paper with 10-15 ml of hot hydrochloric acid and then wash the paper with hot water. Dilute the solution to 150-200 ml, add 2 ml of tartaric or citric acid, 3-4 gm of ammonium chloride, 5 gm of ammonium oxalate, and 3 or 4 drops of methyl red indicator. Neutralize the solution with 1:1 ammonium hydroxide until the solution just turns yellow. Heat just below boiling for 20-30 minutes and filter through a No. 42 Whatman filter paper. Wash the paper and precipitate first with a warm 0.1 percent solution of ammonium oxalate and then six to eight times with hot water. Reserve the precipitate for the determination of calcium.

Combine the filtrates from the oxalate separations. Evaporate to 300 ml, make slightly acid with hydrochloric acid, cool to room temperature and add enough diammonium phosphate as crystals or a freshly prepared 10 percent solution to provide at least a tenfold excess and preferably 1 gm in addition, for each 100 ml of solution. While stirring the solution vigorously, add ammonium hydroxide slowly until the solution is just alkaline and then add 10 ml excess for every 100 ml of solution. Stir for 5 minutes, let stand for 4 hours and filter through a No. 42 Whatman filter paper. Wash the paper and precipitate with a hot 5 percent ammonium hydroxide solution. Discard the filtrate and washings. Dissolve the precipitate in warm dilute (1:4) hydrochloric acid, wash the beaker and stirrer with the acid and transfer the solution to a 250-ml beaker. Dilute to 100-150 ml, add 1 gm of tartaric acid and 0.1 to 0.3 gm of diammonium phosphate. Add ammonium hydroxide drop by drop with constant stirring until the precipitate has formed and the solution is neutral. Add 5 ml excess ammonium hydroxide for each 100 ml of solution, stir for 5 minutes and let stand for at least 4 hours. Filter through a fresh No. 42 Whatman filter paper and wash with a cool 5 percent ammonium hydroxide solution. Transfer the paper and precipitate to a weighed platinum or alundum crucible, dry, char, and ignite. Record the weight of the precipitate.

CALCULATIONS

$$\% \text{ MgO} = \frac{\text{wt. ppt}}{\text{wt. sample}} \times 0.36226 \times 100$$

$$\text{gm/l MgO} = \frac{\text{wt. ppt.}}{\text{sample volume taken, ml}} \times 0.36226 \times 1000$$

If no precipitate is obtained, the magnesium oxide content should be reported as "less than" the minimum amount detectable, a figure based on the actual weight or volume of the sample taken. Assuming the minimum amount detectable is about 3 milligrams then the value to report would be,

$$\text{for solids, } \% \text{ MgO} = \text{less than } \frac{0.003 \times 0.3623 \times 100}{\text{wt. sample}};$$

$$\text{for solutions, gm/l MgO} = \text{less than } \frac{0.003 \times 0.3623 \times 1000}{\text{aliquot taken}}.$$

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The Colorimetric Determination of Manganese as Permanganate using Periodate Oxidation

METHOD Mn-1

SCOPE

This method is intended for the determination of manganese in ores, products and reagents (3).

RANGE

The method as described will determine 0.02% or 0.02 gm/l MnO_2, but can easily be extended to as low as 0.001% or gm/l.

OUTLINE

The colour of the permanganate ion provides a sensitive and specific means for the determination of manganese. It shows maximum absorption at 525 mμ. The best reagents for oxidizing manganese to this form are sodium or potassium periodate (1).

$$2Mn^{++} + 5IO_4^- + 3H_2O \longrightarrow 2MnO_4^- + 5IO_3^- + 6H^+$$

The reaction proceeds rapidly in hot solution. Nitric or sulphuric acid provide suitable media. The reaction rate increases as the acid normality is raised above 2 N. However a 2 N solution is preferred since there is some tendency for incomplete colour development with traces of manganese at the higher acidities (2). Phosphoric acid is beneficial since it prevents precipitation of manganese iodates and periodates and reduces interference due to iron.

Reducing substances interfere by converting permanganate back to manganic or manganous ion. Chloride in particular is deleterious, but sulphite, nitrite, the halides and such organic anions as oxalate must also be absent. These are mainly removed by evaporation with sulphuric and nitric acids.

Chromium III is oxidized and is coloured, but does not interfere if the colour is read at 575 mμ. Cerium III is also oxidized, but does not interfere. Uranyl ion does not absorb above 520 mμ.

APPARATUS

Beakers, Griffin low form:	250 ml.
Beaker covers:	
Graduated cylinders:	25 ml.
Flasks, Erlenmeyer:	250 ml.
Pipettes, volumetric:	1, 2, 5 and 10 ml.

62314-0—25

Flasks, volumetric:	100 ml, 250 ml and 500 ml.
Funnels, filtering, Bunsen long-stem:	65 mm. dia.
Steam bath:	
Spectrophotometer or colorimeter:	
Spectrophotometer cells:	
Burette:	10 ml micro-burette.

REAGENTS

Nitric acid, concentrated:	
Nitric acid, dil.:	1:1 (v/v).
Hydrochloric acid, concentrated:	
Sulphuric acid, dil.:	1:1 (v/v).
Phosphoric acid, concentrated:	
Hydrogen peroxide, 30%:	
Hydrofluoric acid-boric acid mixture:	Add 20 ml of 48% aqueous hydrofluoric acid to 180 ml of a saturated aqueous solution of boric acid and mix. The mixture can be stored in glass bottles.
Potassium periodate solution, 3%, (use hot):	Prepare as needed by dissolving 3 gm KIO_4 in 100 ml water.
Standard manganese solution, 1 ml = 0.05 mg Mn:	Dissolve 0.0500 gm high purity manganese in 10 ml dil nitric acid and boil to expel brown fumes. Cool, dilute to 1 litre in a volumetric flask and mix. The solution need not be standardized. Alternatively, dissolve 1.44 gm $KMnO_4$ in about 200 ml of water, add 20 ml dil (1:1 v/v) sulphuric acid and reduce the permanganate with hydrogen peroxide. Boil to decompose the excess peroxide, cool, and transfer to a 1 litre volumetric flask. Dilute to the mark and mix. Standardize volumetrically.

Preparation of the Calibration Graph

To each of a series of 250-ml Erlenmeyer flasks, add 15 ml of the hydrofluoric-boric acid mixture, followed by 15 ml distilled water, 15 ml nitric acid and 5 ml phosphoric acid. Heat at about 80° C. for a few minutes until all brown fumes are expelled.

Transfer (by means of a micro-burette) aliquots containing 0.025 to 0.45 mg Mn to separate flasks, omitting the addition in the case of the flask which is to serve as the reference blank.

To each flask, add 10 ml of hot 3% potassium periodate solution and boil for 20 minutes to develop the colour. Cool, transfer to 100-ml volumetric flasks, dilute to volume (with *distilled*, not deionized water) and mix.

Measure absorbance of the standards against the reference blank in 1-cm cells at 525 mμ and at 575 mμ. Plot absorbance as ordinate against mg Mn per 100 ml as abscissae, drawing up a separate graph for each wave length.

PROCEDURE

A. Preliminary Preparation

1. *Solid Samples*

Weigh a suitable sample (containing 0.1 to 0.7 mg Mn) into a 250-ml beaker. Add 10 ml nitric acid, cover and boil 10 minutes. If decomposition is not complete, add 10 ml hydrochloric acid, cover and boil again. Add 10 ml dil sulphuric acid (1:1), remove the cover and evaporate to fumes, Cool, wash down the sides with about 10 ml water and take to fumes again. Finally evaporate nearly to dryness. Redissolve the residue in nitric acid using a few drops of hydrogen peroxide if necessary. Filter and wash the paper with hot water. Transfer to a volumetric flask of appropriate size and make to volume.

2. *Solution Samples*

Transfer a suitable aliquot to a volumetric flask of appropriate size and dilute to volume.

B. Colour Development

Place 15 ml of hydrofluoric acid-boric acid mixture in a 250-ml Erlenmeyer flask. Add 15 ml distilled water, 15 ml nitric acid and 5 ml phosphoric acid. Heat at about 80° C. for a few minutes to expel any brown nitrous fumes.

Pipette a suitable aliquot (Table 1) of the sample solution into the flask. Add 10 ml of hot potassium periodate solution and boil for 20 minutes. Cool, transfer to a 100-ml volumetric flask and dilute to 100 ml with *distilled* (not deionized) water.

Prepare a reagent blank solution at the same time using the same aliquot of sample solution, but do not add the potassium periodate solution.

Table 1

Dilution Table for Solid Samples

Range %	Sample Wt. gm	Dilute to ml	Take ml
0.02 – 0.20	2	100	10
0.20 – 1.0	1	100	10
1.0 – 5.0	1	250	5
5.0 – 10.0	1	500	5

Dilution Table for Solutions

Range gm/l	Sample Vol. ml	Dilute to ml	Take ml
0.02 – 0.20	2	do not dilute	
0.20 – 1.0	1	do not dilute	
1.0 – 5.0	10	250 ml	5 ml
5.0 – 10.0	10	500 ml	5 ml

Transfer a portion of the coloured solution to a 1-cm cell and read at 525 mμ (575 mμ if chromium may be present) against the prepared blank solution. Determine the mg MnO_2 per 100 ml solution from the previously prepared calibration graph (for the proper wave length) and record the result.

CALCULATIONS

$$\% \ MnO_2 = \frac{\text{mg } MnO_2 \text{ (graph)}}{1000 \times \text{sample wt.}} \times \frac{\text{final dilution}}{\text{aliquot taken}} \times 100$$

$$\text{gm/l } MnO_2 = \frac{\text{mg } MnO_2 \text{ (graph)}}{1000 \times \text{sample vol.}} \times \frac{\text{final dilution}}{\text{aliquot taken}} \times 1000$$

If no colour is obtained, report the result as "less than" the minimum amount detectable, an actual figure based on the sample weights and aliquots used, rather than using the term "not detected".

The minimum amount of manganese detectable may be taken as 0.1 mg and the figure to report would be

$$\% \ MnO_2 = \text{less than } \frac{0.1}{1000 \times \text{sample wt.}} \times \frac{\text{final dilution}}{\text{aliquot taken}} \times 100$$

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The Colorimetric Determination of Molybdenum in Ores and Mill Products

METHOD Mo-1

SCOPE

The thiocyanate-stannous chloride procedure described here is easily carried out and is the most useful general method for the determination of molybdenum.

RANGE

Amounts of molybdenum in excess of 0.0001% can be readily determined.

OUTLINE

In acid solution quinquevalent molybdenum forms a coloured complex with thiocyanate in the presence of stannous chloride. This complex can be extracted by organic solvents such as butyl acetate (1) and isoamyl alcohol (2) (3). If the amber complex is not extracted, the colour will fade slowly upon standing. Chromium is removed by fuming with hydrochloric and perchloric acids. Vanadium interference is eliminated by reduction with stannous chloride during the second wash step. This also removes any slight interference from uranium (4, 5). The use of fluoride to complex titanium has been investigated, but found to be without significant effect (5). Titanium must be present in considerable amounts (50 times the molybdenum content) to cause significant errors (3).

The colour intensity is increased in the presence of iron. Maximum colour intensity is reached when 1 milligram of iron is present for every 30 micrograms of molybdenum. The presence of considerably larger quantities of iron is without further effect (4).

Moderate quantities of common contaminants do not affect the colorimetric method when an extraction has been made. Such conditions as acidity, concentration of reagents and volume of sample before extraction, should be controlled fairly rigidly for best results.

The colour is stable over a period of at least 4 hours. The presence of perchlorates tends to stabilize the colour.

Perchloric acid, used in this method, reacts violently with organic matter when hot. Condensation of perchloric acid in the fume hood can result in explosions or fires, if organic matter is volatilized in the same hood at any time. Perchloric acid must be used only in hoods set aside for that purpose. Safety glasses must be worn.

Mo-1

APPARATUS

Separatory funnels:	Squibb type, 60 ml size.
Fisher safety centrifuge:	
Centrifuge tubes:	15 ml size.
Beckman Model "B" spectrophotometer:	
Spectrophotometer cells:	1 cm light path.

REAGENTS

Standard molybdenum solution:	Dissolve 0.8 grams of molybdic acid (85% MoO_3) in 15 ml of 1:1 ammonium hydroxide and dilute to 1 litre with distilled water. Take a 5 ml aliquot and dilute to 500 ml with distilled water. 1 ml of the latter solution contains approximately 4.4 micrograms molybdenum. Standardize the molybdenum solution as follows:—acidify 50 ml of the solution with acetic acid, heat to boiling and precipitate the molybdenum as lead molybdate by adding lead acetate solution until a small excess is present. Allow the precipitate to settle (keep warm) for 30 minutes. Filter the precipitate on a tared Gooch crucible, washing with 2% ammonium nitrate solution. Ignite the precipitate at 550°–600° C and weigh as lead molybdate. Lead molybdate × 0.2613 = molybdenum.
Lead acetate solution, 4%:	Dissolve 10 grams of lead acetate in water, add acetic acid to remove any white turbidity and dilute the solution to 250 ml with distilled water. Filter before use.
Hydrochloric acid solution, 2%, v/v:	20 ml concentrated HCl to 1 litre with water.
Ferric sulphate solution, 2%:	Dissolve 10 grams of ferric sulphate ($Fe_2(SO_4)_3 \cdot 6H_2O$) in distilled water, acidify with hydrochloric acid and dilute to 500 ml with distilled water. 1 ml contains approximately 4 milligrams of iron.
Sodium thiocyanate solution, 5%:	Dissolve 25 grams sodium thiocyanate in distilled water and dilute to 500 ml. *Note:* The use of potassium thiocyanate in the procedure may result in the formation of insoluble potassium perchlorate.
Stannous chloride solution, 14%:	Dissolve 70 grams of stannous chloride ($SnCl_2 \cdot 7H_2O$) in 50 ml of hydrochloric acid, and dilute to 500 ml with distilled water.
Stannous chloride-sodium thiocyanate wash solution:	Mix 10 ml of 14% stannous chloride solution, 10 ml of 5% sodium thiocyanate solution and 10 ml of concentrated hydrochloric acid. Dilute to 100 ml with water and saturate with n-butyl acetate.
N-butyl acetate:	Reagent grade, saturated with 5% sodium thiocyanate solution.

Preparation of Standard Curves

Take aliquots of the standard molybdenum solution containing 4 to 40 micrograms Mo. Carry these through the procedure outlined for solution samples, using a reagent blank. Draw up a graph with optical density as ordinate and micrograms Mo per 10 ml n-butyl acetate as abscissa.

(NOTE: 48γ Mo in 10 ml n-butyl acetate in 1-cm cell gives an absorbancy of about 1.0 at 470 mμ).

PROCEDURE

1. *Solid Samples*

Weigh one or more grams of the sample (Table 1) into a 250-ml beaker. Dissolve in 5 ml hydrochloric acid, 5 ml nitric acid and 5 ml perchloric acid,

finally taking the sample to dense fumes. Cool, wash down the sides of the beaker with distilled water and fume the sample a second time.

Take up the soluble salts in 2-3 ml hydrochloric acid and 25-50 ml water and filter off the insoluble residue on a Whatman No. 40 filter paper, collecting the filtrate in a volumetric flask of appropriate size (Table 1). Wash the residue and paper with 2% hydrochloric acid solution. Dilute the filtrate and washings to the mark with distilled water. Pipette an aliquot (Table 1) into a 60-ml separatory funnel and add 1 ml of 2% ferric sulphate solution (4 mg of iron). Add 2 ml of perchloric acid, neutralize the sample with ammonium hydroxide (until the ferric hydroxide precipitate just begins to form). Add exactly 2 ml of hydrochloric acid, cool the solution to room temperature and adjust the volume to 25 ml, using a gummed paper strip or wax pencil mark on the funnel as a guide. Add, by pipette, 10 ml of 5% sodium thiocyanate solution. Mix, add 10 ml of 14% stannous chloride, and again mix well. Add, by pipette, 10 ml of n-butyl acetate, and shake the mixture for 1 or 2 minutes. Separate the aqueous layer and wash the organic layer twice with 20-ml portions of the stannous chloride wash solution (20 seconds each time). Draw off the organic layer into a 15-ml centrifuge tube and centrifuge for 1 minute. Read against a reagent blank carried through the procedure on the Beckman Model "B" spectrophotometer using a wave length of 470 mμ (no filter) and 1-cm Corex cells.

2. *Solution Samples*

Pipette a suitable volume of the sample (Table 1) into a 250-ml beaker. Add 2 ml of concentrated nitric acid and 5 ml of concentrated perchloric acid,

Table 1

Table of Dilutions for Molybdenum Determination

Solid Samples

Range % Mo	Sample Wt. take	First Dilution Dilute to	Second Dilution	Aliquot take
1.0 – 10.0	1 gram	500 ml	5/250	10 ml
0.1 – 1.0	1 gram	250 ml	10/100	10 ml
0.01 – 0.1	2 grams	250 ml	—	10 ml
0.001 – 0.01	2 grams	100 ml	—	10 ml

Solution Samples

Range gm/l	Sample Wt. take	First Dilution Dilute to	Second Dilution	Aliquot take
1.0 – 10.0	10 ml	500 ml	5/250	10 ml
0.1 – 1.0	10 ml	250 ml	10/100	10 ml
0.01 – 0.1	10 ml	250 ml	—	10 ml
0.001 – 0.01	25 ml	100 ml	—	10 ml

and take to fumes. If organic matter is present, repeat this treatment till it is destroyed. Transfer to a suitable volumetric flask. Pipette an appropriate aliquot (Table 1) into a 60-ml separatory funnel, and continue the procedure as outlined for solid samples.

CALCULATIONS

$$\% \text{ Mo} = \frac{\gamma \text{ Mo/10 ml (graph)}}{1{,}000{,}000} \times \frac{\text{1st dil.}}{\text{aliq. taken}} \times \frac{\text{2nd dil.}}{\text{aliq. taken}} \times \frac{100}{\text{sample wt.}}$$

$$\text{gm/l Mo} = \frac{\gamma \text{ Mo/10 ml (graph)}}{1{,}000{,}000} \times \frac{\text{1st dil.}}{\text{aliq. taken}} \times \frac{\text{2nd dil.}}{\text{aliq. taken}} \times \frac{1000}{\text{sample vol.}}$$

If the sample gives approximately the same reading as the blank, the amount of Mo shall be reported as less than the minimum amount detectable (an actual figure based on the sample weights and volumes used). The minimum amount detectable may be considered as 1 microgram of Mo per 10 ml and the figure to report may be calculated on this basis, for example:

$$\% \text{ Mo} = \text{less than } \frac{1}{1{,}000{,}000} \times \frac{\text{1st dil.}}{\text{aliq. taken}} \times \frac{\text{2nd dil.}}{\text{aliq. taken}} \times \frac{100}{\text{sample wt.}}$$

References

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The Flame Photometric Determination of Soluble Sodium and of Total Sodium in Ores, Mill Products and Solutions

METHOD Na-1

SCOPE

The method is primarily used for establishing a reagent balance for sodium salts in connection with the sodium carbonate leaching process. In conjunction with suitable decomposition methods it is also used for the determination of the total sodium content of ores.

RANGE

The actual concentration range of the solution used for analysis is 0.005 to 0.05 gram Na/l. Solutions of higher concentrations are diluted to a concentration in this range. The lower limit for soluble sodium in ores and residues would therefore be about 0.005% (5-gram sample). The limit for total sodium would be approximately 0.01%. (0.1% if the J. Lawrence Smith decomposition method is used.)

OUTLINE

The method is based on the photoelectric measurement of the spectral emission of sodium at 588-589μ using oxy-acetylene flame excitation.

With a good monochromator, such as that in the Beckman instrument, interference by emission of other elements is unlikely. However, absorption of energy from the flame for emission at the wave lengths characteristic of the interfering elements may occur, resulting in a diminution of that available for emission by the sodium ion (i.e. a form of quenching). In careful work this is avoided by removing the commoner interfering elements by a combined carbonate-hydroxide precipitation. For routine determinations of soluble sodium compounds in essentially similar samples this refinement can be eliminated once the extent of quenching has been determined. This may be ascertained by means of a suitable calibration curve, prepared by "spiking" samples with increasing amounts of sodium.

For the determination of total sodium in ores, the J. Lawrence Smith fusion (1) is used. This is a method for decomposing silicates by means of calcium oxide and calcium chloride which are formed by the reaction of calcium carbonate and ammonium chloride. The calcium displaces the alkali in the alkali silicate producing calcium silicates and alkali chlorides. Magnesium is eliminated since it is precipitated by the calcium hydroxide formed when the sample is taken up in water.

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APPARATUS

Flame photometer:	Beckman Model "B" Spectrophotometer with Beckman 9125 flame attachment. Carefully read instructions (2 and 3) before attempting to turn on or use the instrument.
Acetylene tank regulator, two stage, with gauges:	The low-pressure acetylene regulator gauge must have a total range not exceeding 30 lb., with a danger mark at 15 lb. (the pressure must never exceed this value). Fisher Cat. No. 10-565 is suitable.
Oxygen tank regulator, two stages with gauges:	The low-pressure oxygen regulator gauge must have a total range of at least 50 lb. Fisher Cat. No. 10-564 is suitable.
Exhaust system:	This consists of a sufficient length of 4" dia. flexible metal tubing suspended over the burner and connected to a 100 cfm exhaust fan. The exhaust can be directed out a window, or into a fume hood.
Crucibles, platinum, J. Lawrence Smith or 30 ml high form:	
Transite board, ¼":	
Timer, 120 minute type, with alarm:	
Beakers, Vycor 250 ml, (well used Pyrex beakers can also be used):	
Watch glasses, Pyrex (well used):	
Burette, 50 ml:	
Beakers, 5 ml:	
Pipettes, 10 ml:	
Volumetric flasks:	50 ml, 100 ml, 250 ml, 1000 ml.

REAGENTS

Acetylene, 250 cu ft cylinder:	The burner uses 5 cu ft of acetylene per hour, or about 1 cu ft for every 2-4 samples. The tank should be replaced when the pressure falls to 75 psi.
Oxygen; 200 cu ft cylinder:	The burner uses 8 cu ft of oxygen per hour, or about 1 cu ft for every 1-2 samples. Never turn the oxygen setting down while the burner is in operation, as an economy measure. The fuel may be turned down or the flame shut off completely, if there is a period of 15 minutes or more between analyses.
Ammonium chloride CP:	
Calcium carbonate CP, low alkali:	
Ammonium carbonate CP:	
Ammonium hydroxide CP:	
Hydrochloric acid 6N:	
Hydrochloric acid 5%:	
Sulphuric acid CP:	
Sulphuric acid 1:5:	
Hydrofluoric acid CP:	
Whatman No. 41 filter paper:	

Standard Sodium Solution A, (for spiking) 5 mg Na per ml:	
Standard Sodium Solution B, 100 mg Na per ml:	
Standard Sodium Solution C, 50 mg per ml:	prepared fresh using Solution B.
Standard Sodium Solution D, 30 mg per ml:	prepared fresh using Solution B.
Standard Sodium Solution E, 10 mg per ml:	prepared fresh using Solution B.

PROCEDURE

A. Preliminary Treatment

1. *Sodium (Soluble in Dilute Acid) in Ores and Carbonate-Leach Residue*

Weigh a suitable sample (*see* Table 1) into a 250-ml Vycor beaker. Moisten with water, then add 50 ml of 5% hydrochloric acid and cover the beaker with a well-used Pyrex watch glass and boil 15 minutes. Filter through a Whatman No. 41 filter paper, and wash the residue with a minimum of hot water. Transfer to a volumetric flask of appropriate size (Table 1) and make to volume at room temperature.

If quenching is suspected *see* "Spiking Technique", Section B(2).

2. *Total Sodium in Ores and Residue*

(a) *Decomposition with acids (Note: Carry out a reagent blank).*—Weigh a suitable sample into a 250-ml Vycor beaker, moisten with water, and add 6N hydrochloric acid until no more effervescence occurs. Transfer the solution and any residue to a platinum dish and evaporate to dryness (if carbonates are absent, weigh the sample into the platinum dish directly and omit the hydrochloric acid attack). Add 10 ml of 1:5 sulphuric acid, followed by 10 ml of hydrofluoric acid, and evaporate to dense fumes on a padded hot plate.

Remove the beaker from the hot plate, let cool, and add 50 ml of distilled water. Cover with a well-used Pyrex watch glass and heat till all the salts are in solution. Transfer to a 250-ml Vycor beaker, using a minimum of hot water. Add a few ml of concentrated ammonium hydroxide and add a solution of 2 gm ammonium carbonate in 25 ml water. Boil and let the precipitate settle.

Filter the solution (Whatman No. 41 H paper) into a 250-ml Vycor beaker and wash the precipitate with hot water. Evaporate the combined filtrate and washings to dryness on the steam bath. Carefully heat the dried residue over a burner to expel ammonium salts. Cool. Dissolve the residue in 25 ml of 5% hydrochloric acid. Transfer to a volumetric flask of appropriate size (Table 1) and make to the mark at room temperature.

(b) *J. Lawrence Smith Decomposition (Note: Carry a reagent blank through the whole procedure.)*—Weigh out 0.5 gm of the finely ground sample in a 100-ml porcelain casserole and mix very intimately with 0.5 gm pure ammonium chloride.

Weigh out 4.0 ± 0.1 grams of low-alkali CP calcium carbonate. Mix about 3 grams of this with the sample mixture and transfer to the special J. Lawrence Smith crucible, or if this is not available, to an ordinary 30-ml platinum crucible with a well fitting lid, first spreading on the bottom of the crucible, a layer of calcium carbonate from the 1 gram reserved. Use the remaining carbonate to remove any adherent ore in the casserole and add this to the crucible.

Insert the Smith crucible into a piece of nearly vertical transite through a hole of such a size that three-quarters of the crucible projects through the board. If an ordinary crucible is used, the bottom third should extend below the board, and in this case the board should be horizontal.

Cover the crucible, and if an ordinary crucible is used, put a 50-ml beaker of water on top to provide the necessary cooling to prevent loss of volatile alkali chlorides.

Heat the crucible until it is just red and keep it at this temperature for 15 minutes. When ammonia is no longer liberated, increase the heat until the lower section of the crucible is bright red and keep it at this temperature for 45 minutes. Then cool the crucible and add enough water to cover the residue. Rinse off the cover and wash the residue into a 250-ml Vycor beaker. Add water to give a volume of about 50 ml and let the mass disintegrate. Boil a few minutes and filter into another 250-ml Vycor beaker (leaving the bulk of the residue in the original beaker). Repeat the extraction of the residue, making sure it is thoroughly disintegrated. Wash the paper with hot water using the minimum volume necessary. (Test the residue for complete decomposition by adding dilute hydrochloric acid, in which it should dissolve completely). Discard this residue.

Add a few ml of concentrated ammonium hydroxide followed by a solution of 2 gm ammonium carbonate in 25 ml water to the warm sample solution. Boil, then let the precipitate settle.

Filter the solution into a 250-ml Vycor beaker and wash the precipitate well with hot water. Evaporate the combined filtrate and washings to dryness on a steam bath. Carefully heat the dried residue over a burner to expel the ammonium salts. Cool, dissolve the residue in 25 ml of 5% hydrochloric acid. Transfer to a volumetric flask of appropriate size (*see* Table 1) and make to the mark at room temperature.

B. Measurement of Sodium Content

1. *Regular Technique*

For routine analysis of a large number of samples which are all of the same basic composition, prepare a series of standards covering the anticipated range of the samples, by adding appropriate amounts of "Standard Sodium Solution A" to a sodium-free matrix solution, of the same composition as the samples, so that when diluted to the proper range for analysis, the standards from which the standard curve is drawn will have the same matrix composition as the samples. If the composition of the matrix is unknown, it is sometimes possible to scan a number of samples qualitatively, and choose the one with lowest sodium content to use as a matrix, determining its sodium content by the "Spiking Technique" Section B(2). Standard sodium solution can then be added to this sample and a standard curve drawn up.

In either case, determine the emission reading for each standard as described in Section C. Plot a graph with sodium content in mg/l as abscissa against emission reading as ordinate.

Determine the flame emission of the suitably diluted samples. At the same time, run two of the standard samples used in preparing the standard curve, which bracket the sodium content of the samples, to verify that conditions are the same as when the curve was prepared. Record the emission reading, correct for the reagent blank and read the sodium content of the solution from the graph. Calculate the sodium content of the sample as described under "Calculations".

2. *Spiking Technique*

(a) *Solid Samples*—If quenching is suspected, carry through a duplicate sample, to which sufficient standard sodium solution is added (from a burette) to approximately double the sodium content of the final solution. Alternatively, if the sodium content is high enough, make up a preliminary dilution of the sample solution obtained from a single sample, to e.g., 50 ml, and take two 10-ml aliquots. To one of these, add sufficient standard sodium solution to approximately double the sodium content.

(b) *Solution Samples*—Take two aliquots of the solution and carry out the preliminary acidification and other treatment. To one, add sufficient standard sodium solution to approximately double the sodium content, and then dilute both to the same volume, as required.

In the case of both solid and solution samples, dilute an equivalent amount of the pure sodium solution as was used for spiking the sample, to the same final dilution. Run the sample, the spiked sample and the pure sodium solution on the flame photometer as in the regular procedure and record all three readings (designated A, D and M respectively,—*see* "Calculations".)

C. Operation of the Flame Photometer

WARNING: Except when lighting the flame, keep the hands completely out of the housing, whenever the flame is burning. Do not use, or allow others to use, ether or other inflammable solvents while the flame is on. *Always* keep the exhaust duct over the flame and make sure the fan is running. Always turn the oxygen on first and off last to prevent damage to the burner. In case of an accident of any kind, immediately close the fuel tank valve.

Carefully read the instruction manuals (2 and 3) before using the instrument. The following abbreviated instructions are intended only as a step-by-step guide and refresher for use by operators familiar with the instrument. *See* Figures 1A and 1B for identification of the various controls.

Stepwise Operating Procedure

1. Turn the "Sensitivity Multiplier" to the "Stand by" position.
2. Turn the "Shutter Control" to SHTR.
3. Verify that the blue-sensitive phototube (range 320-625 millimicrons) and the 10,000 megohm resistor are installed in the phototube compartment.
4. Connect the instrument to the power line.
5. Turn the "Power Switch" to ON.
6. Let the instrument warm up for at least 15 minutes. Maximum stability is obtained after a warm-up of 45 minutes; however, operation may be started after 15 minutes if the dark current is adjusted before each measurement.

During the warm-up period, transfer suitable portions of the properly-diluted sample and standard solutions to the special 5-ml beakers, laid out on a marked paper grid to simplify identification.

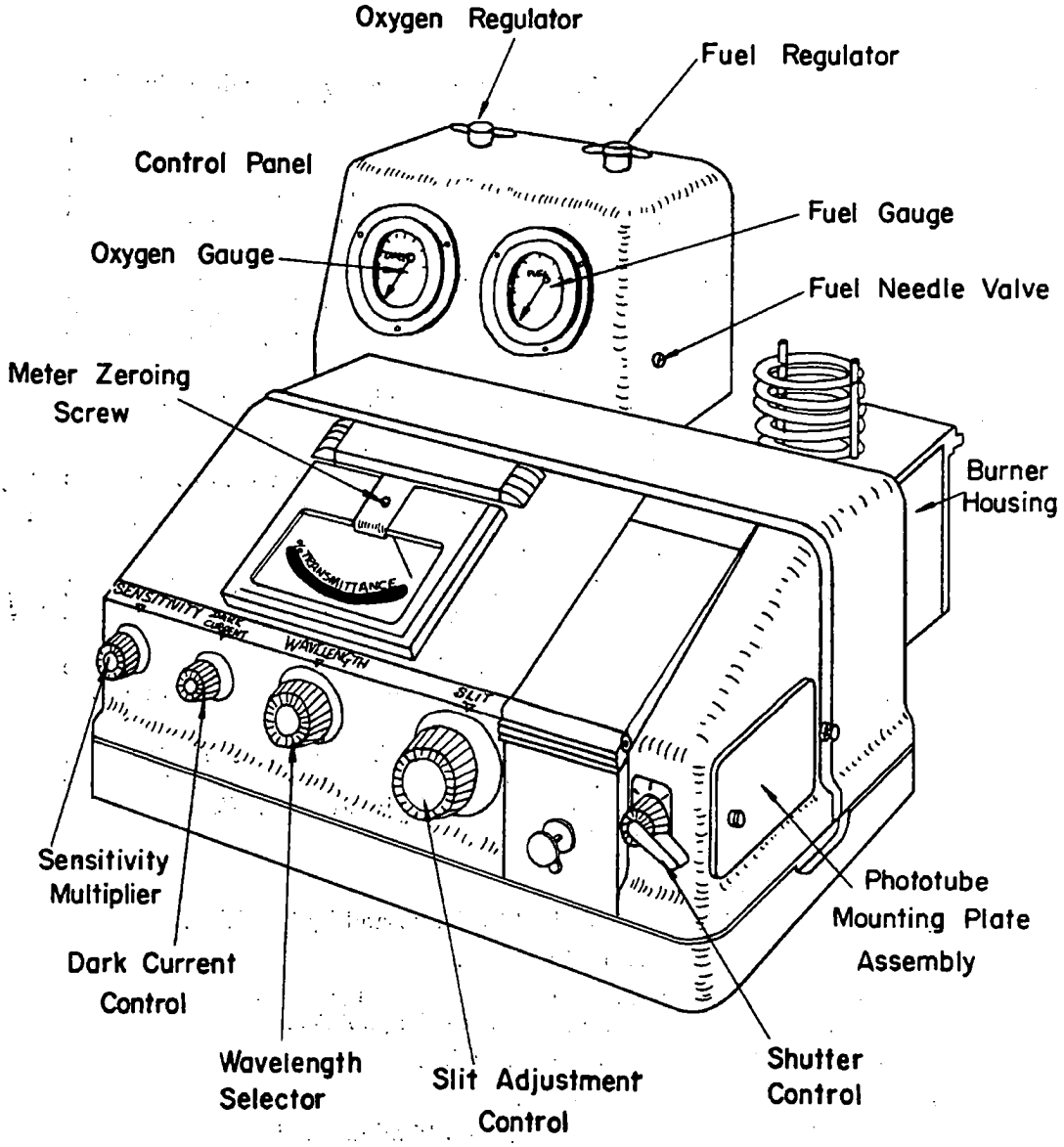

Figure 1A

BECKMAN B FLAME SPECTROPHOTOMETER

Front View

7. Turn the "Sensitivity Switch" to 3 and balance the meter needle at zero with the "Dark Current Control".

8. Close the regulators on the control panel.

9. Open the tank valves and adjust the tank regulator to 30 to 50 psi for oxygen and 5 to not over 10 psi for fuel.

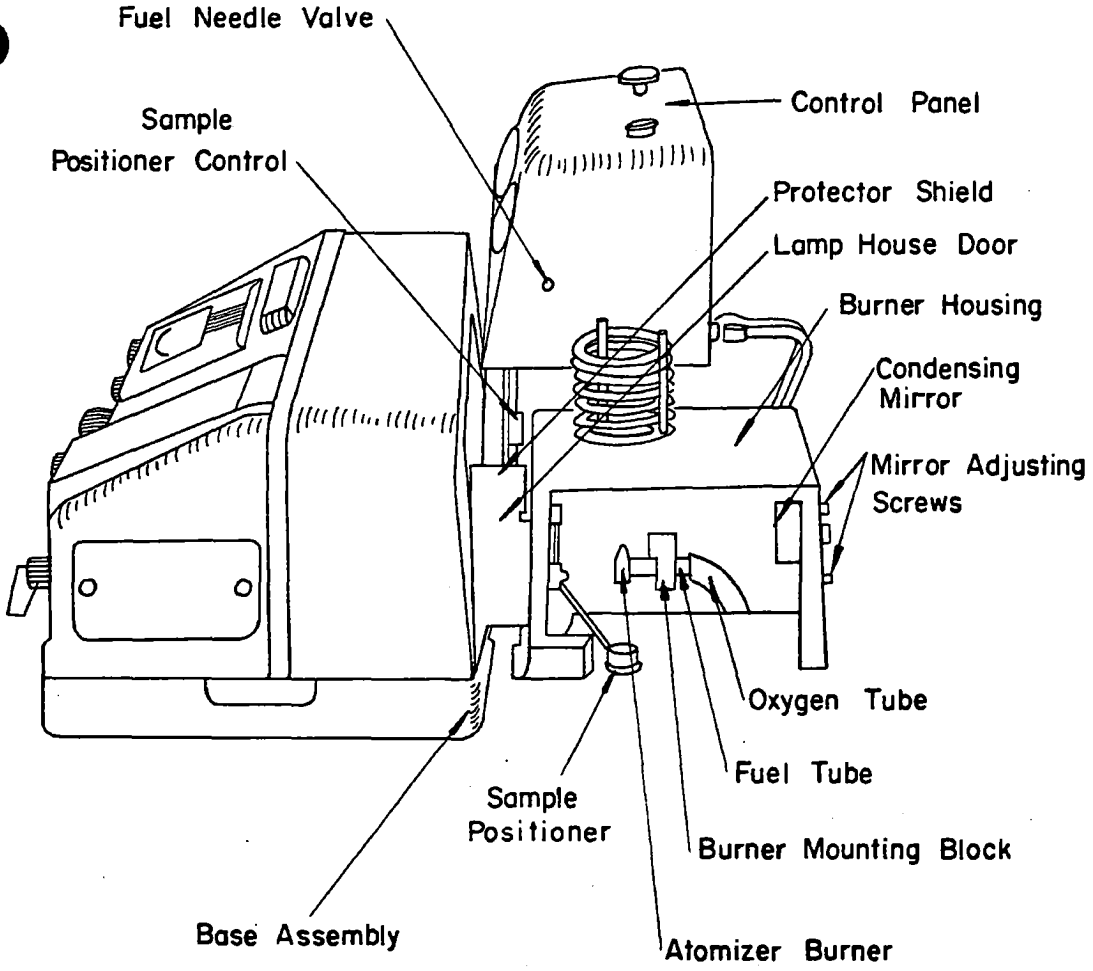

Figure 1B

BECKMAN · B FLAME SPECTROPHOTOMETER

Side View

10. Open the oxygen regulator on the control panel to the pressure designated on the burner tag. *Check, to make sure there is a full oxygen flow from the burner before turning on the fuel.*

11. (a) *Flame Adjustment*—(This step is required only when setting up the burner). Open the burner-housing door, carefully open the fuel regulator on the control panel to 3 to 5 psi, and light the burner by applying a lighted match next to and just below the tip of the burner. Adjust the fuel needle valve to provide a flame with the visible blue portion about 2 or 3 inches high, but not above the chimney hole. Adjust the regulator on the control panel to determine the best fuel pressure between 3 and 5 psi. In determining the best fuel pressure there is a point below which there is an abrupt change in the shape of the flame, and the fuel pressure should be kept above this value. Do not, however, turn the fuel pressure up to the point where a white streak appears in the lower part of the blue flame. Having obtained the required flame appearance, carry out subsequent adjustment using the fuel needle valve to obtain the optimum excitation conditions described below.

Fill one of the 5-ml sample beakers with the "Standard Sodium Solution C" (50 mg Na/l) and move it under the capillary by rotating the sample positioner control. The resulting yellow flame should be 2 to 2½ inches high, with one-eighth of an inch diameter blue and yellow hemisphere of flame covering the burner top. This hemisphere should be continuous and steady, and in contact with the burner throughout its circumference. Adjust the fuel needle valve to obtain a flame of this description. If the rate of solution consumption is too fast (more than 1.5 to 2.0 ml per minute) small tongues or spattering in the flame will occur. In this case, reduce the oxygen pressure a pound or two. Similarly if the rate is too slow, increase the oxygen pressure or investigate the burner capillary to ensure it is not clogged. During operation close the housing door. Note the control panel settings and record them for routine use.

(b) *Regular Operation*—Open the fuel regulator on the control panel to the pressure determined in step 11. (a). Open the burner housing door, and light the burner by applying a lighted match to and just below the tip of the burner. Using Standard Sodium Solution C, check the burner operation, particularly as regards solution consumption, which should be 1.5 to 2.0 ml per minute. If the burner does not give this performance, clean it. If satisfactory performance is still not obtained, repeat the flame adjustment, step 11. (a).

12. Using Standard Sodium Solution C, set the wave length dial at the peak sodium line emission by opening the shutter and moving the dial in the region 585-600 millimicrons until maximum meter response is obtained.

13. With Solution C still in place, adjust the slit width control to give a reading of about 75% transmittance. (If the instrument is properly aligned this will correspond to a slit width of about 0.35 mm.) Check the dark current setting and then record the meter reading of the standard. If the needle fluctuates (not more than 0.5% of the reading) record the average position.

Close the shutter, raise the door and remove the beaker.

14. Place a beaker containing "Standard Sodium Solution D" (30 mg Na/l) in the sample holder. Check the dark current, open the shutter and record the meter readings.

15. Close the shutter, remove the beaker, and repeat step 14, using "Standard Sodium Solution E".

16. Close the shutter, remove the beaker of standard solution and replace with a beaker of distilled water. Raise this into position and allow the water to

spray until a colorless flame is obtained. Open the shutter and record the meter reading as "flame background". (Should be less than 1%.)

17. Close the shutter, replace the water beaker with the beaker of the sample solution. Read the emission as above.

18. If a spiked sample was prepared, read this now.

19. Finally, read the reagent blank.

20. Repeat the readings of Standards C, D and E and average the results of each (corrected for flame background).

21. Continue alternating standards, samples, and flame background determinations, until all the samples have been read.

22. Finish off by running a flame background determination (since this cleans out the burner at the same time). Close the shutter, and remove the beaker.

23. Turn the flame down, *first closing the fuel tank regulator*, then after a minute, the oxygen tank regulator. Then close the tank valves. Allow the system to flush itself out, then close the control panel regulators. Always check and blow out the flame, if necessary.

Table 1

Dilution Table for Solid Samples

Range % Na	Take gm	Dilute to ml
below 0.05%	5	50
0.05 to 0.20	2	100
0.20 to 1.0	1	250
1.0 to 5.0	1	1000

Table 2

Dilution Table for Solutions

Range gm/l Na	Take ml	Dilute to ml	Take 2nd aliquot ml	Dilute to
0.005 to 0.05	do not dilute		—	—
0.05 to 0.5	10	100	—	—
0.5 to 5.0	10	1000	—	—
5.0 to 50	10	1000	10	100

CALCULATIONS

1. *Regular Method*

For Solids:

$$\% \text{ Na} = \frac{\text{Na Conc'n from graph (mg/l)}}{1000} \times \frac{\text{final sol. vol. ml}}{1000} \times \frac{100}{\text{sample wt.}}$$

For Solutions:

$$\text{gm/l Na} = \frac{\text{Na Conc'n, graph (mg/l)}}{1000} \times \frac{\text{final sol. vol.}}{\text{aliquot}} \times \frac{\text{1st dil. vol.}}{\text{sample vol.}}$$

2. *Spiking Technique*

$$\text{mg Na/l} = \frac{A \times M \times C}{D - A}$$

where A = meter reading of unknown (corrected for reagent blank)

D = meter reading for spiked unknown (corrected for reagent blank)

M = meter reading for concentration of pure Na solution equivalent to that added in spiking (corrected for flame background)

$$C = \text{Calibration Constant} = \frac{M}{(Na)}$$

(Na Concentration, mg/l, per meter reading unit)

For Solids:

$$\%\ \text{Na} = \frac{\text{Na Conc'n (mg/l)}}{1000} \times \frac{\text{final sol. vol. (ml)}}{1000} \times \frac{100}{\text{sample wt.}}$$

For Solutions:

$$\text{gm/l Na} = \frac{\text{Na Conc'n (mg/l)}}{1000} \times \frac{\text{final sol'n vol.}}{\text{aliq.}} \times \frac{\text{initial dil'n vol.}}{\text{sample vol.}}$$

REPORTING RESULTS

In reporting sodium results, always distinguish the assay according to the method by which the sodium was brought into solution. If the dilute acid treatment only was used, report as "% Soluble Sodium". If the sample was completely dissolved, report "% Total Sodium".

References

1. Smith, J. Lawrence: *Am. J. Sci.* (2) **50**, 1871, in "Applied Inorganic Analysis" 2nd ed., Hillebrand, Lundell, Hoffman and Bright. 1953, New York, John Wiley and Sons.
2. Beckman Bulletin 291A: Beckman Model B Spectrophotometer.
3. Beckman Bulletin 278: Beckman Model B Flame Spectrophotometer.

Rapid Colorimetric Determination of Niobium in Ores using Thiocyanate and Ether Extraction

METHOD Nb-1

SCOPE

The method outlined may be used to determine the niobium content of rocks containing elements that usually interfere with the peroxide method for niobium. It may also be used to determine niobium in concentrates, precipitates and solutions, but here the hydrogen peroxide-sulphuric acid method may be preferred (2).

RANGE

Ores containing niobium in excess of 0.03% Nb_2O_5 may be analyzed employing this method. The accuracy of the determination of niobium in high-grade ores may suffer because of dilution errors introduced in order that the final volume contains less than 30 micrograms of Nb_2O_5.

OUTLINE

In acid solution niobium forms a coloured complex with thiocyanate in the presence of stannous chloride. This complex can be extracted with ether. If the yellow complex is not extracted immediately, the thiocyanate polymerizes and some of the niobium is lost (1).

The method permits the determination of 30 micrograms of niobium in the presence of 1000 micrograms of iron, titanium or uranium, of 500 micrograms of vanadium or of 100 micrograms of tungsten and/or molybdenum (1), (3).

The interference of vanadium is prevented by extraction of the thiocyanate complexes with ether prior to reduction with stannous chloride. The iron is subsequently removed by reduction with stannous chloride. The addition of acetone inhibits the polymerization of thiocyanate ion and establishes the niobium thiocyanate complex (1). Molybdenum is excluded in the acid attack when phosphoric acid is used. Moreover it has been found that, in the presence of uranium, low niobium values are obtained if the bisulphate decomposition is used, while the hydrofluoric acid-phosphoric acid attack gives substantially quantitative results (4).

The thiocyanate reaction is carried out in solutions 4 molar in hydrochloric acid and 0.5 molar in tartaric acid and the thiocyanate complex is concentrated by extraction with ether. The extract is washed with stannous chloride and absorbancy measurements are made at 385 millimicrons. Actual quantities are then read from a previously prepared standard curve (1).

APPARATUS

Platinum dishes:	50 ml, flat bottom.
Funnels, separatory:	60 ml size.
Flasks volumetric:	100 ml size and 10 ml size.
Crucibles, silica or quartz:	
Beckman Model B Spectrophotometer:	
1 cm Corex cells:	

REAGENTS

Ethyl ether—peroxide free:	The ether should be shook with 1/10 of its volume of 10% stannous chloride solution the day it is to be used.
Ammonium thiocyanate solution:	20 grams in 100 ml water. Prepare fresh daily.
HCl-tartaric acid mixture:	15 grams of tartaric acid dissolved in 100 ml of 9 M hydrochloric acid.
Stannous chloride solution:	10 grams of $SnCl_2 \cdot 2H_2O$ dissolved in 100 ml of 2 M hydrochloric acid. Prepare fresh every second day.
Sodium pyrosulphate:	Reagent grade sodium bisulphate, fused and ground in a mortar.
Tartaric acid, 1 M solution:	151 grams of reagent grade tartaric acid per litre.
Niobium solution:	Fuse 100 mg of niobium oxide (Nb_2O_5) or the equivalent, with 4 grams of fused sodium pyrosulphate (that has been ground in a mortar) in a 30 ml silica or quartz crucible. When cool, dissolve the melt in 1M tartaric acid and dilute to the mark in a 500 ml volumetric flask with 1M tartaric acid (Note 1).

Preparation of Calibration Curve

Transfer suitable aliquots of the niobium solution containing from 1 to 30 micrograms of Nb_2O_5 (Note 2) to 60-ml separatory funnels. Add 5 ml of HCl-tartaric acid solution reagent by pipette, then 5 ml of ammonium thiocyanate solution by burette followed immediately by 5 ml of peroxide-free ether added by pipette. Without delay shake the flask for 30 seconds (timed). When the layers have completely separated, drain off and discard the lower aqueous phase and add 2 ml of stannous chloride solution to the ether layer. Shake again for 10 seconds, allow the phases to separate, drain off the lower aqueous phase and add 2 ml of stannous chloride solution to the ether layer. Shake again for 10 seconds, allow the phases to separate and drain off the lower phase. Repeat the treatment of the ether with stannous chloride if necessary (Note 3). Transfer the ether phase to a 10-ml volumetric flask, add acetone to the mark and mix. Determine the optical density of the extracts against a reagent blank prepared in the same manner as the niobium-bearing extracts, at a wave length of 385 millimicrons on the Beckman "B" spectrophotometer using 1-cm Corex cells and a filter. Plot a graph with optical density as abscissa and micrograms of Nb_2O_5 per 10 ml volume as ordinate.

PROCEDURE

A. Decomposition

1. *Fusion Method (Uranium Absent)*

Place about 4 gm of fused sodium pyrosulphate (that has been ground in a mortar) in a 30-ml silica or quartz crucible. Add 0.2 gm of sample and mix well. Add 5-6 drops of concentrated sulphuric acid, cover the crucible and carefully

fuse the mixture over a Fisher-type burner. When the melt is quiet or it appears that the sample has been decomposed, cool the crucible and contents. Place the crucible and lid in a 250-ml beaker and add about 50 ml of 1M tartaric acid. Heat and stir until the fusion cake has dissolved. Transfer the solution to a volumetric flask of appropriate size (usually 100 ml) without filtering and dilute to the mark with 1M tartaric acid. A 1.0-ml aliquot of this solution is taken for colour development in Section B.

2. *Acid Method* (4) (*Uranium Present*)

Place 0.2-1.0 gram sample into a platinum dish (50-ml flat bottom type), add about 1 ml of syrupy phosphoric acid, 10 ml of hydrochloric acid and 10 ml of hydrofluoric acid. Evaporate the mixture on the hot plate with mild heat at first, then at a medium heat until only a paste of phosphoric acid remains. (Do not fume or take to dryness). Wash the contents of the dish into a volumetric flask (100-ml) with 1M tartaric acid and dilute to the mark with 1M tartaric acid. A 1.0-ml aliquot of this solution is taken for colour development in Section B.

B. Colour Development

Transfer a 1.0-ml aliquot of the solution (Note 2) to a 60-ml separatory funnel. Add 5 ml of HCl-tartaric acid solution reagent by pipette, then 5 ml of ammonium thiocyanate solution by burette followed immediately by 5 ml of peroxide-free ether added by pipette. Without delay shake the flask for 30 seconds (timed). When the layers have completely separated, drain off and discard the lower aqueous phase. Add 2 ml of stannous chloride solution to the ether solution. Shake for 10 seconds, allow the phases to separate and drain off and discard the lower phase. Repeat the treatment of the ether layer with stannous chloride, if necessary (Note 3). Transfer the ether phase to a 10-ml volumetric flask, add acetone to the mark and mix. Determine the optical density of the yellow-coloured extract at a wave length of 385 millimicrons on the Beckman "B" spectrophotometer using 1-cm Corex cells and a filter. It is necessary to carry a reagent blank and one or more standard niobium samples through the colour development as a safeguard against deteriorated reagents, etc. Determine micrograms of Nb_2O_5 per 10 ml volume by means of the previously prepared calibration graph.

CALCULATIONS

$$\% \, Nb_2O_5 = \frac{\gamma \text{ Nb per 10 ml (from graph)}}{1{,}000{,}000} \times \frac{\text{final solution volume}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

If the sample gives approximately the same reading as the blank, the amount of niobium oxide (Nb_2O_5) should be reported as less than the minimum amount detectable (an actual figure based on the sample weight and volumes used) rather than using the term "not detected". The minimum amount detectable may be considered as 3 micrograms Nb_2O_5 per 10 ml volume for colorimetric readings using 1-cm cells and the figure to report may be calculated on this basis, i.e.

$$\% \, Nb_2O_5 = \text{less than } \frac{3}{1{,}000{,}000} \times \frac{\text{final solution volume}}{\text{aliquot taken}} \times \frac{100}{\text{sample weight}}$$

Notes

(1) Solutions containing niobium must be at least 1M in tartaric acid in order to prevent hydrolysis of niobium which occurs quite readily.

(2) The amount of tartaric acid present has an effect on the colour intensity of the niobium-thiocyanate complex. Therefore it is necessary to have the same amount of tartaric acid in each separatory funnel, for samples, standards and the blank.

This becomes important if, for example, it is found that too small an aliquot has been taken for the final dilution, and the optical density is too low for accurate reading. To take a larger aliquot will necessitate the use of similar aliquots of the standard and blank solutions. For this reason, use of a more concentrated final solution volume is preferred to taking a larger final aliquot.

(3) The stannous chloride wash is repeated until the colour intensity appears constant. All extracts should be washed with stannous chloride the same number of times.

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The Volumetric Determination of Amines in Amine-Kerosene Solution

METHOD NH_2-1

SCOPE

This method is intended for the determination of amines used for solvent recovery of uranium and thorium. Coupled with volume determinations of the organic layer, and kerosene determination (METHOD Ke-1), it can be used to assess solvent losses.

RANGE

The method will detect as little as 0.05 gm/l of amine in kerosene.

OUTLINE

Organic amines behave as strong bases in glacial acetic acid solution and can be titrated by standard solutions of strong acids in the same solvent. The end-point is sharp and can be detected using methyl violet as an indicator, or electrometrically using the glass electrode with a calomel reference half-cell (1).

The presence of water is deleterious. It can be sufficiently removed by adding about 90% of the theoretical amount of acetic anhydride. The full amount is not used in order to avoid having an excess of acetic anhydride, which can react with primary and secondary amines causing erroneous results and a poor end-point. Large amounts of inert solvents, such as kerosene, interfere with the end-point, but the amounts ordinarily associated with the sample have little effect. The amine must be in the free base form (2). In the case of solvents that have been in use for uranium recovery, therefore, the sample should be taken from the final stripper if carbonate or caustic stripping is used. Otherwise, the kerosene solution must be converted to the free base form by stripping and shaking with carbonate solution prior to titration.

Since the amines used are commercial products consisting of mixtures of closely related amines, the average molecular weight will vary from batch to batch. In checking amine loss, it is therefore necessary to standardize the acid against amine from the actual batch in use. It is convenient to set aside a portion of the original amine solution for this purpose.

APPARATUS

Funnels, separatory, Squibb pear-shaped:	125 ml size.
Beakers, Griffin low form:	250 ml and 100 ml sizes.
Funnel rack:	
Millivoltmeter:	A pH meter calibrated in millivolts will serve.
Glass and calomel electrodes:	

REAGENTS

Perchloric acid 0.1N, standard:	Dissolve 8.5 ml perchloric acid (70%) in 900 ml glacial acetic acid. Add 20 ml of acetic anhydride and let stand overnight before using. Standardize as described below.
Perchloric acid 0.01N, and 0.005N:	Prepared by diluting appropriate quantities of the above solution with glacial acetic acid.
Methyl violet indicator:	0.2 gm methyl violet in 100 ml of o-chlorobenzene.

Standardization of Acid

Put 0.5 gm potassium acid phthalate (primary standard) in 60 ml of glacial acetic acid. Reflux the mixture to dissolve the salt. Cool, add 2 drops methyl violet and titrate with perchloric acid to first disappearance of the violet tinge.

PROCEDURE

Prepare a standard solution of the amine to be determined in kerosene (or take a portion of the original unused kerosene-amine solution set aside for this purpose). Carry aliquots of this solution covering the required range through the procedure, to permit standardization of the standard perchloric acid in terms of the amine in question.

Take a quantity of the sample sufficient for two or three titrations (e.g. 25 ml) and transfer to a 125-ml separatory funnel.

Extract the amine twice, for about 2 minutes each time, with an equal volume of 2M ammonium nitrate solution, discarding the aqueous layer each time. Then extract it twice, for about 2 minutes each time, with an equal volume of sodium hydroxide. Finally wash several times with distilled water till the washings are neutral, discarding the washings. Filter the amine through a dry paper into a dry 100-ml beaker.

Pipette an aliquot containing 2-4 meq. (1 ml of pure amine or 10 ml of kerosene solution = 2 to 2.5 meq.) into a 250-ml beaker. Add 100 ml glacial acetic acid. Add 2 drops of methyl violet indicator and titrate with 0.1N perchloric acid solution in a 50-ml burette until the colour of the solution changes from purple to light green. Alternatively, use glass and calomel electrodes, and a millivoltmeter, and titrate to -0.55 mv.

For more dilute amine solutions use the more dilute standard perchloric acid solution.

CALCULATIONS

$$\text{gm/l amine} = \frac{T_a \times N_a \times M_o}{\text{Sample taken, ml}}$$

where T_a = ml standard perchloric acid solution used

N_a = normality of perchloric acid

M_o = molecular weight of amine (determined by titration of a weighed amount)

References

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The Determination of Aliphatic Amines in Solutions from Solvent Extraction Recovery Processes

METHOD NH_2-2

SCOPE

The method is intended for use in estimating solvent losses in amine solvent extraction processes. It is applicable to all the amines used in these processes.

RANGE

Amine concentrations as low as 0.005 gm/l (as NH_3) can be detected using 1-cm cells. This corresponds to 0.008 ml tri iso-octyl amine per litre. Concentrations down to 0.0015 ml per litre could be determined using 5-cm cells.

OUTLINE

A Kjeldahl digestion converts amine nitrogen to ammonia which is separated and determined by the colorimetric procedure described below (1). If ammonia or polyamide flocculents (e.g. Separan) are suspected to be present they can be removed by refluxing in the presence of excess caustic. The caustic hydrolyzes the amide and converts any ammonium salts to ammonia, which can then be volatilized. Use of reflux serves to retain the amines which are otherwise somewhat volatile with steam. After this treatment the solution is neutralized with sulphuric acid. (If these compounds are known to be absent, the step should be omitted).

In either case, the raffinate is then treated by the Kjeldahl digestion procedure (2). This step involves prolonged heating of the sample with concentrated sulphuric acid in the presence of selenium as a catalyst (3). Selenium dissolves in the concentrated sulphuric acid to produce Se. SO_3 and it is believed that the co-ordination of selenium on the sulphur trioxide activates the latter so as to promote the subsequent reactions (4). As a result, the carbon and hydrogen of the amine are oxidized to carbon dioxide and water, some of the sulphur trioxide being reduced to sulphur dioxide. The amine group is not oxidized, however, but is instead converted to ammonium sulphate (7). The ammonia is liberated by caustic treatment as before and steam-distilled. The distillate is made to volume and an aliquot taken for the colorimetric ammonia determination. This is based on the blue colour formed when sodium phenate is added to a solution of ammonia that has been treated with hypochlorous acid (5).

Primary, secondary and tertiary amines may be determined, (but not distinguished) by the method. It may also be adapted to the determination of amides and nitrates (6).

Sampling

A serious difficulty in determining the organic solvents in raffinates arises due to the tendency of the organic liquid to preferentially wet glass, resulting in

losses in the sample bottle and in the glassware used in aliquotting. For this reason it is recommended that the sample be taken in a tared Kjeldahl flask, and the sample size determined by weighing, calculating the volume taken from the specific gravity of the solution. This flask is then used for the actual determination.

APPARATUS

Steam-distillation apparatus consisting of:	*See* Figure 1, METHOD NH_3-1.
Flask, boiling, flat bottom:	1 litre size.
Flask, Kjeldahl, Fisher-Rieman long neck, with ₹ 34/45 joint:	500 ml size, similar to Fisher Cat. No. 10-113.
Spray trap, Kjeldahl Iowa State type:	
Condenser, West, plain:	300 mm size.
Adapter, distillation:	
Receiving flask, Erlenmeyer, glass stoppered:	300 ml size.
Burners, gas, Bunsen type:	
Adapters, reducing, for Rieman-Kjeldahl flask:	34/45 male ₹. 24/40 female ₹.
Condenser, West ₹, drip tip joint 24/40:	300 mm long.
Pipettes:	1 to 10 ml sizes.
Volumetric flasks:	25 ml and 250 ml.

REAGENTS

Sulphuric acid, concentrated CP:	
Sodium sulphate:	
Selenous acid:	
Sodium hydroxide:	
Ammonia-free water:	prepared by passing tap water through a mixed-bed ion exchange demineralizer, just before use. Distilled water usually contains ammonia.
Sodium hydroxide, 40% solution:	Dissolve 40 gm sodium hydroxide in 100 ml of ammonia-free water. Store in polyethylene bottles.
Ammonium sulphate standard solution:	Dissolve 1.940 gm $(NH_4)_2 SO_4$ in water and dilute to 500 ml. 1 ml = 0.001 gm NH_3. Dilute 10 times for use as a standard.
Hypochlorous acid reagent:	Bubble chlorine into ice-cold water until an excess of solid chlorine hydrate forms. *Keep under refrigeration.* Approx. life, 2-3 weeks.
Sodium phenate reagent:	Add a cold solution of sodium hydroxide (7.2 gm NaOH in 300 ml water) to 16.7 gms of commercial phenol, and shake until the latter is dissolved. Keep under refrigeration. Approx. life, 2-3 weeks.
Manganous chloride solution, 0.003M:	0.06 gm $MnCl_2 \cdot 4H_2O$ in 100 ml water.

Preparation of Standard Curve

Pipette 10 ml of the diluted standard ammonia solution (0.001 gm NH_3) into a Kjeldahl flask containing 100 ml of ammonia-free water. Assemble the steam-distillation apparatus (Figure 1, METHOD NH_3-1) and carry through the steam-distillation step ("Procedure", Section D), adding 10 ml of 40% w/v sodium hydroxide solution. Dilute the distillate to 250 ml for a concentration of 4μ gm NH_3 per ml. Take aliquots of the distillate containing 4 to 20 μ gm NH_3 and carry these through the colour development ("Procedure", Section E). Prepare a graph with optical density as ordinate and micrograms ammonia per 25 ml as abscissa.

PROCEDURE

A. *Taking the Sample*

Collect 100 ml of sample in a tared flask section of a 500-ml Rieman-type Kjeldahl flask. Weigh to determine the amount of sample taken, dividing by the specific gravity to obtain the volume in ml. If the sample contains ammonia or polyamide-type flocculents, proceed with Section B below. If these compounds are absent omit this Section and proceed directly to Section C, "Kjeldahl Digestion".

B. *Removal of Ammonia and Polyamide Interference*

Mount the flask containing the sample on a retort stand, add 10 ml of 40% w/v sodium hydroxide solution and insert a ⅋ reducing adapter (male 34/45, female 24/40). Connect a ⅋ 24/40 West condenser and with water flowing through the condenser, commence heating the flask with a gas flame. Adjust the flow of water through the condenser so that the sample refluxes to a point about half-way up the column. Continue refluxing until no blue colour is produced on a strip of moist red litmus paper held to the open end of the condenser (test for ammonia). Remove the condenser and adapter, cool, and neutralize cautiously with a few ml of concentrated sulphuric acid.

C. *Kjeldahl Digestion*

To the contents of the flask add 20 ml concentrated sulphuric acid, 10 gm of sodium sulphate and 0.5 gm selenous acid. Insert the ⅋ neck of the flask, and mount the flask on a retort stand at a 30° angle from the vertical, in a well-ventilated fume hood. Support the bottom of the flask in a hole in a piece of asbestos board, the hole being of such a size that the bottom of the flask projects through to the level of the liquid in it (so that the flask will not be heated above the liquid level). Heat the flask gently using a gas burner until it is evaporated to about one-half its original volume (50 ml). Place a short-stem funnel in the top of the neck of the flask. Still using a low flame, heat until charrings occurs, and continue heating gently until the resulting carbonaceous matter begins to clear up. Then gradually increase the temperature until the acid boils gently and the liquid becomes colorless or nearly so. Continue heating for a further 10 or 15 minutes.

D. *Steam Distillation*

Cool and rinse down the funnel and neck of the flask. Cautiously add 75 ml of ammonia-free water, shaking to dissolve any salts that have solidified, and cool the flask under the tap. Assemble the distillation apparatus, connecting

the steam generator to the flask and attaching a spray trap, condenser and a receiving flask containing about 25 ml of ammonia-free water (Figure 1, METHOD NH_3-1).

Adjust the tip of the adapter on the condenser so that it is just below the surface of the water in the receiving flask. Put about 500 ml of dilute sulphuric acid (20 ml 1:1 v/v sulphuric acid in 500 ml of water) in the steam generator and heat to boiling.

When all the preparations are complete, remove the stopper from the Kjeldahl flask, quickly pour 90 ml of cold 40% w/v sodium hydroxide solution into it, and re-insert the stopper. These operations must be performed with a minimum of delay to prevent loss of ammonia. Make sure all the connections are tight and a steady stream of cold water is running through the condenser. Gently shake the contents of the Kjeldahl flask to mix them, and light the burner under it. Adjust the flame on both burners so that liquid does not build up in the Kjeldahl flask and to give a rate of distillation of about 4 ml per minute. Continue the distillation until about 200 ml of distillate have been collected. Lower the receiver so that the end of the adapter is out of the distillate and remove the flame from the flask. Disconnect the condenser from the spray trap and rinse down the inside of the condenser and adapter into the receiving flask using ammonia-free distilled water. Transfer the distillate to a 250-ml flask and dilute to volume with ammonia-free water.

E. *Colour Development*

Transfer an aliquot of the distillate containing 20 μ gm NH_3 or less to a 25-ml volumetric flask and dilute to about 15 ml with ammonia-free water. Add 2 ml of hypochlorous acid reagent, mix and let stand 5 minutes. Add 2 drops of manganous chloride solution, followed by 2 ml of phenate reagent. Mix, make to volume with ammonia-free water, and mix again. Let stand 15 minutes and measure the intensity of colour at 620 mμ in 1-cm cells on the Beckman Model B spectrophotometer.

CALCULATIONS

gm/l Amine (in terms of ammonia)

$$= \frac{\gamma NH_3 \text{ (from graph)} \times 250 \times 1000}{1{,}000{,}000 \times \text{aliquot taken for colour} \times \text{sample vol.}}$$

gm/l as Tri iso octyl amine

$$= \frac{\gamma\ NH_3 \text{ (from graph)} \times 250 \times 1000 \times 353}{1{,}000{,}000 \times \text{aliquot taken} \times \text{sample vol.} \times 17 \times .8189}$$

If the sample contains no detectable ammonia, report the result as "less than" the minimum detectable using the sample and dilutions employed.

References

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The Colorimetric Determination of Certain Secondary and Tertiary Amines in Solvent Extraction Raffinates

METHOD NH_2-3

SCOPE

An accurate knowledge of solvent losses, whether due to solubility of the active ingredient or caused by insufficient settling time (i.e. entrainment), is of major importance in the operation of a solvent extraction plant for metal recovery The amine solvent extraction process for the recovery of uranium employs hydrocarbon (varsol or kerosene) solutions of long chain aliphatic secondary and tertiary amines, and this method permits the estimation of the total amine lost to the raffinate. Combined with the kerosene determination (METHOD Ke-1) it permits complete evaluation of solvent losses.

RANGE

This method will detect as little as 0.005 ml of tri iso octylamine per litre of raffinate, using spectrophotometer cells with a 5-cm light path. The sensitivity is about half of this for secondary amines of comparable molecular weight (e.g. Rohm and Haas LA-1). Primary amines (e.g. Primene JMT, and the secondary amine di(tridecyl P) amine), do not give a colour with the reagents.

OUTLINE

The method is based on the formation of an amine-thiocyanato cobalt complex by the reaction of divalent cobalt and alkali thiocyanate with the amine in weakly acid sulphate solution(2). Developed primarily for the determination of cobalt, it has been modified by Ashbrook, of Eldorado Mining and Refining Ltd., (Research and Development Laboratories), to give an extremely convenient method for amine determinations (1). The coloured complex can be extracted from the aqueous solution by a number of immiscible organic solvents such as carbon tetrachloride, butyl acetate, amyl acetate and isoamyl alcohol. The colour, which is pure blue in the oxygenated solvents, and turquoise in carbon tetrachloride, has maximum absorption at a wave length of 620 mμ. Carbon tetrachloride is the preferred solvent since, being heavier than water, it forms the lower phase and hence does not contact the ferric phosphate precipitate which floats in the aqueous phase, thus further reducing the possibility of iron interference. It also simplifies withdrawing the organic layer as it is not necessary to rinse the stem of the funnel before drawing off the organic layer. The principal interferences are stated to be Ni(II), Fe(III), Bi, V(IV), U(VI), and Cu(II). Cr(VI) and Mn(II) interfere slightly, while Mo(VI) and W(VI) are without effect (2, 4, 5).

Of these, Ni(II) and Cu(II) occur so rarely in uranium liquors as to require no special consideration in the present method. If Ni(II) should ever be present,

it is possible to eliminate its interference by using potassium cyanate instead of potassium thiocyanate, with only small loss in sensitivity (3). Copper (II) can be reduced with sulphite or thiosulphate (2, 5).

The ferric and uranyl ions, which are the principal interfering ions in raffinates, are best masked by the use of fluoride or phosphate (1, 2). In practice, it is found that the gelatinous ferric fluoride hinders phase separation in the extraction step so that in most cases sodium phosphate is the preferred complexing agent. In the case of highly acid solutions it is difficult to obtain a high enough concentration of phosphate ion due to the formation of the acid phosphate ion and phosphoric acid. As a result the use of the more highly ionized fluoride salt would be preferable for solutions which are more than 1 normal in hydrogen ion (1).

The principal difficulty with the method lies in obtaining a reproducible sample and this is a problem from the point of removing the raffinate sample from the circuit, up to the pipetting of the sample for analysis. The entrained organic solution is not uniformly distributed in the aqueous phase, it tends to float to the top on standing, and it wets glass preferentially. It is therefore recommended that the sample be taken from a point in the circuit where it can be agitated, and that as large a sample bottle as possible be used to give a high volume/surface ratio. In the procedure given, also, the pipette is rinsed five times with the solution before pipetting out the aliquot for analysis, to equilibrate the inside surface and prevent excessive loss of organic solution. As an alternative, a dry pipette can be used without the preliminary rinsing and the pipettes rinsed at the end with a few ml of methanol.

APPARATUS

Shaker, mechanical:	Eberbach or equivalent
Pipettes, volumetric:	0.5, 5 and 25 ml sizes
Cylinders, graduated:	10 and 25 ml sizes
Separatory funnels, Squibb:	125 ml size
Separatory funnel rack:	double tier
Funnels, filtering, Bunsen long stem:	65 mm diameter, smooth
Bottles, weighing, tall-form, glass stoppered:	30 ml size
Spectrophotometer (with red-sensitive phototube):	
Spectrophotometer cells:	1 cm and 5 cm light path
Burette, micro:	5 ml size
Flask, volumetric:	500 ml

REAGENTS

Sodium phosphate, monobasic:	
Cobalt-thiocyanate solution:	Dissolve 15 gm of cobalt nitrate and 10 gm of sodium thiocyanate in 100 ml of water.
Carbon tetrachloride:	
Methanol:	
Standard amine:	The concentrated amine which is the one to be detected, or better, the kerosene-amine solution from the circuit, whose amine concentration has been determined by METHOD NH_2-1.

Standard amine solution: Pipette 0.5 ml of the amine, or a corresponding volume of the amine-kerosene solution (10 ml for a 5% solution) into a 500-ml volumetric flask and make to volume:—1 ml = 0.001 ml of amine

Sulphuric acid, 3%: v/v

Preparation of the Spectrophotometric Calibration Curve

Transfer 0.1- to 2.0-ml aliquots of the standard amine solution to 125-ml separatory funnels. Add 25 ml of 3% sulphuric acid and 25 ml of water. Mix, add 5 gm of sodium phosphate and shake for 1 minute. Add 20 ml of the cobalt-thiocyanate solution, mix and let stand 2 minutes. Finally add 10.0 ml of carbon tetrachloride and shake vigorously for 2 minutes. Let settle, draw off the carbon tetrachloride through a dry Whatman No. 31 paper into a clean, dry, tall-form weighing bottle and stopper immediately.

Measure the optical density at 620 mμ using 1-cm and 5-cm cells and the red sensitive phototube, against a blank of carbon tetrachloride. Plot a calibration curve of optical density readings against ml of amine for both cell path lengths.

PROCEDURE

Shake the sample bottle, (which should be 1 litre or more if possible), vigorously for 10 minutes on a shaker. Rinse a dry 25-ml pipette five times with the sample. Pipette a 25-ml portion of the sample into a separatory funnel and add 25 ml of water. Add 5 gm of monobasic sodium phosphate and shake for 1 minute. Add 20 ml of the cobalt-thiocyanate solution, mix well and let stand 2 minutes. Finally, add 10.0 ml of carbon tetrachloride and shake vigorously for 2 minutes. Allow the layers to separate. Draw off and filter the carbon tetrachloride through a dry Whatman No. 31 filter paper into a clean, dry, 30-ml, tall-form weighing bottle and stopper immediately. Measure the optical density of the solution at 620 mμ using 1-cm or 5-cm cells and a red sensitive phototube, against a carbon tetrachloride blank. Record the reading. Determine the volume of amine (ml) in the sample aliquot taken by reference to a standard curve for the amine in question and record this value also.

CALCULATION

$$\text{ml amine/litre} = \frac{\text{ml amine (from graph)} \times 1000}{25}$$

If no reading is very low, report the amine content as "less than" the limit of detection, an actual figure based on the sensitivity of the method for the amine in question. Base this figure on the assumption that an optical density of less than 0.05 is not significant.

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The Colorimetric Determination of Ammonia

METHOD NH_3-1

SCOPE

This method is intended for those samples in which the ammonia can be separated into an aqueous solution by a steam distillation.

RANGE

Amounts of ammonia in excess of 0.0025% can be determined.

OUTLINE

The blue colour formed when sodium phenate is added to a solution of ammonia that has been treated with hypochlorous acid forms the basis of a method for the determination of submicro amounts of ammonia (1). The aqueous solution of ammonia in which the colour is formed is obtained by steam distillation, since it has been found here (2) that recovery is more rapid and complete using this technique than it is when direct distillation is used.

The hypochlorous acid reagent decreases in concentration with age and this causes a decrease in the intensity of the colour developed with ammonia. For this reason, standards must be carried through with each batch of samples.

The colour formed is stable for 24 hours. A linear relation exists between the optical density at 620 mμ and ammonia concentration over the range 0 to 1.4γ NH_3 and the method will detect .07γ NH_3.

In spite of the extreme sensitivity of the method, and the large amounts of ammonia usually present in the laboratory atmosphere, the blank correction is low.

For samples containing ammonia in excess of 2%, it can be determined by steam distilling into a known volume of standard acid and titrating with sodium hydroxide (2).

APPARATUS

Steam-distillation apparatus, consisting of:

- Flask, boiling: 1000 ml size.
- Flask, Kjeldahl: 300 ml.
- Trap, Kjeldahl, Iowa State type:
- Condenser:
- Adapter:
- Flask, Erlenmeyer: 300 ml size.
- Burners, gas, Bunsen type:

See Figure 1 for assembly.

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Pipettes:	1 to 5 ml size.
Flasks, volumetric:	25 ml sizes.
Spectrophotometer:	
Spectrophotometer cells:	1 cm light path.

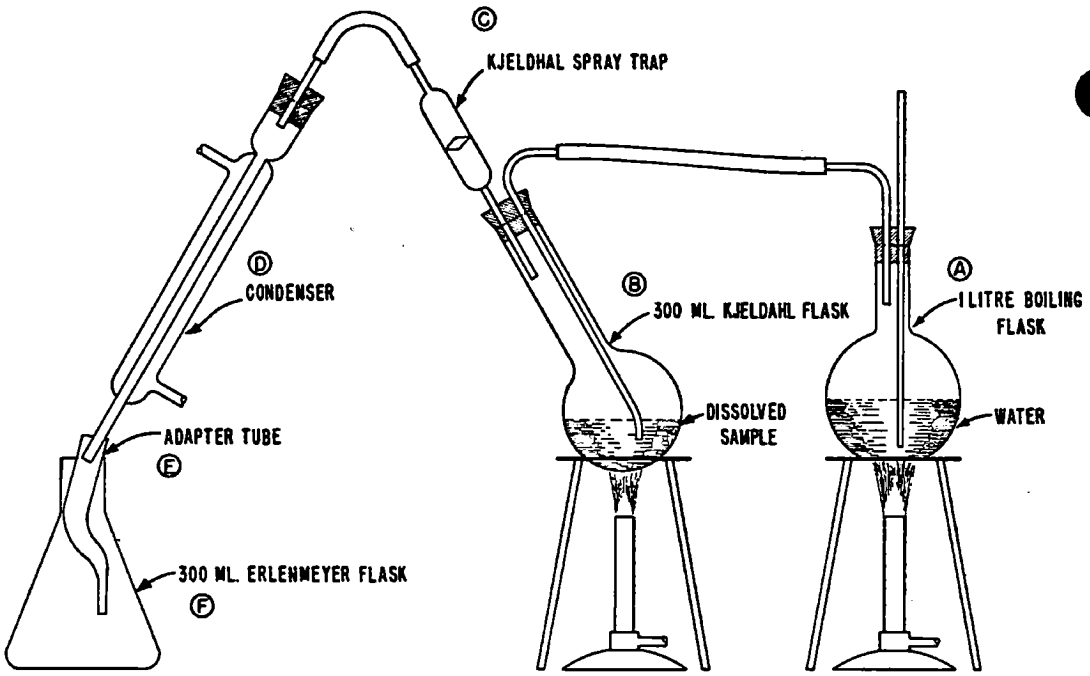

FIG. 1 - AMMONIA STEAM-DISTILLATION APPARATUS.

REAGENTS

Standard ammonium solution:	Dissolve 0.7759 gm of ammonium sulphate $(NH_4)_2SO_4$ in 50 ml of distilled water containing 10 ml 1:1 sulphuric acid and dilute to 1 litre with distilled water. 1 ml of this solution contains .0002 gm of ammonia (NH_3).
Sulphuric acid dil:	1:1 v/v.
Chlorine gas:	lecture bottle.
Sodium hydroxide solution, 40%:	Dissolve 80 gm sodium hydroxide in 200 ml of distilled water.
Hypochlorous acid reagent:	Bubble chlorine gas into ice-cold distilled water until solid chlorine hydrate forms. The approximate chlorine content determined by the iodide-thiosulphate method should exceed 0.05 M chlorine. Store the solution in a refrigerator; approximate life, 2-3 weeks.
Sodium phenate reagent:	Add a cool solution of sodium hydroxide 7.2 gm (0.18 mole) in 300 ml of distilled water, to phenol, 16.7 gm (0.0178 mole) and shake until the latter is dissolved.
Manganous chloride solution 0.003M:	0.39 gm of $MnCl_2$ dissolved in a litre of water.

Hydrochloric acid solution, 0.1N:	8.5 ml concentrated HCl, dilute to 1 litre with distilled water; standardize.
Sodium hydroxide solution, 0.1N:	5 gm NaOH dissolved in distilled water and diluted to 1 litre: standardize.

Standardization of Hydrochloric Acid and Sodium Hydroxide

Standardize the sodium hydroxide solution against potassium biphthalate, $KHC_8H_4O_4$. Obtain the ratio of the volume of hydrochloric acid solution to that of the sodium hydroxide. From this data calculate normality of the HCl solution.

Preparation of Standard Curve

Prepare a standard ammonia solution by substituting 10 ml of ammonium sulphate solution for the sample in the procedure below. Follow the procedure for "Steam Distillation". Dilute the distillate to 500 ml for a concentration of 4μ gm of ammonia per ml. Take aliquots of standard solution containing 4 to 32 micrograms of ammonia and carry them through the procedure for "Colour Development". Draw up a graph with optical density as ordinate and micrograms of ammonia per 25 ml solution as abscissa. Prepare a standard curve each time a set of samples is analyzed.

PROCEDURE

A. Steam Distillation

1. *Ammonia Content <0.01 gm per Sample*

Weigh (or pipette) a sample containing not more than 0.01 gm of NH_3 into a 300-ml Kjeldahl flask. Add 10 ml 1:1 sulphuric acid and 25 ml water. Place a small short-stem funnel in the neck of the flask and mount the flask at a 30° angle from the vertical. Heat gently until the sample is in solution. Cool, rinse down the funnel and neck of the flask with 25 ml distilled water, and cool again. Connect up the distillation apparatus and heat the acidulated water in the steam generator to boiling, (dilute sulphuric acid solution, 10 ml 1:1 H_2SO_4 to 500 ml of distilled water), but do not pass steam through the solution. Place approximately 25 ml distilled water in the receiver flask and adjust the condenser so that the end of the adapter is below the surface of the water. When all is in readiness, quickly pour 40 ml of cold 40% sodium hydroxide into the Kjeldahl flask, and connect the latter in position. Perform operations as quickly as possible to prevent loss of ammonia. Make sure all connecting stoppers are tight and that a steady, rapid stream of cold water is running through the condenser. Gently shake the contents of the flask to mix, and light burners under the flasks. Adjust the flame to maintain a constant volume of solution in the Kjeldahl flask and so that the rate of distillation is about 5 to 8 ml per minute. Continue the steam distillation until about 200 ml of liquid has been collected, then lower the receiver so that the end of the adapter is out of the distillate, and remove the flame from the flasks. Disconnect the Kjeldahl flask from the condenser and flush down the inside of the condenser and adapter. Dilute the distillate to 500 ml with distilled water.

2. *Ammonia Content >0.01 gm per Sample*

The above procedure may be used to determine ammonia in a sample where the concentration is greater than 0.01 gm NH_3. The difference in the method

is as follows: Place 25 ml of standard acid in the receiver flask and collect about 150 ml of distillate. Add a few drops of methyl red indicator and titrate the excess acid in the solution with standard sodium hydroxide.

B. Colour Development

Transfer an aliquot of the ammonia distillate containing not more than 25γ of NH_3 to 25-ml volumetric flask and dilute to approximately 15 ml with distilled water. Carefully pipette 2 ml of hypochlorous acid solution and mix. Allow the solution to stand 5 minutes. Treat each flask individually and add two drops of manganous chloride solution, mix, and pipette carefully 2 ml sodium phenate reagent. Dilute to 25 ml with distilled water and mix well. Allow to stand 20 minutes and read the absorbance of the solution at 620 mμ on the spectrophotometer using 1-cm cells. A reagent blank is used to set the zero on the absorbance scale.

CALCULATIONS

For solid samples:

$$\% \ NH_3 = \gamma NH_3 \text{ per 25 ml (taken from graph)} \times 10^{-6} \times \frac{500}{\text{aliquot}} \times \frac{100}{\text{sample wt.}}$$

For solution samples:

$$\text{gm/l } NH_3 = \gamma NH_3 \text{ per 25 ml (taken from graph)} \times 10^{-6} \times \frac{500}{\text{aliquot}} \times \frac{10^3}{\text{sample wt.}}$$

The minimum amount of ammonia detectable is considered as 1 microgram per 25 ml. If no colour appears, report the result as "less than" a figure based on this amount, e.g.

$$\% \ NH_3 = \text{less than } \frac{1}{10^6} \times \frac{500}{\text{aliquot taken, ml}} \times \frac{100}{\text{sample wt. gm}}.$$

For samples where NH_3 is determined by titration

$$\% \ NH_3 = [\text{ml HCl} - (\text{ml NaOH} \times R)] \times N_a \times \frac{17.03}{1000} \times \frac{100}{\text{sample wt.}}$$

where N_a = normality of HCl

R = ratio HCl/NaOH normalities.

References

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The Gravimetric Determination of Nickel

METHOD Ni-1

SCOPE

This method is principally intended for checking leach solutions to determine whether corrosion of stainless steel equipment is occurring. It is, of course, generally useful for determining nickel in various materials.

RANGE

The lower limit of determination corresponds to 0.001 gm Ni and not more than 0.1 gm should be present in the sample taken for analysis.

The lower limit is set by the solubility of dimethyl glyoxime and for small amounts the colorimetric procedure should be used.

OUTLINE

Nickel forms bright red insoluble salts with ortho-dioximes of the general formula R—C(=NOH)—C(=NOH)—R in neutral, acetic acid or ammoniacal solutions. One of the first and best of these is dimethyl glyoxime (2). The salt has a solubility of less than 0.1 mg in 100 ml cold water, but up to 0.6 mg in hot water (3). Alcohol increases the solubility and since it is used as a solvent for the reagent, a large excess of the latter must be avoided.

The precipitate is anhydrous, readily dried at 110-120°C, and it is not hygroscopic. It may be weighed as such (3).

It is bulky, however, so that not more than 30-50 mg of nickel can be handled.

Iron will, of course, precipitate in the neutral solution used for nickel precipitation. This is avoided by the use of citrate to complex it. Ferrous iron reacts with dimethyl glyoxime to give a soluble red-coloured compound in ammoniacal solution, which will interfere if present in large amounts (4). Since iron will be present in the ferrous state after the hydrogen sulphide precipitation of copper, it should preferably be re-oxidized. It is stated not to interfere if precipitation is carried out in weakly acid medium.

Copper tends to co-precipitate with nickel and consumes reagent so it is best removed (5). This is accomplished by hydrogen sulphide, or by electrodeposition, since nickel is not deposited from acid solution.

Aluminum and chromium interference is avoided by use of citrate to complex them, as with iron.

Bismuth also interferes, but is removed by hydrogen sulphide, and complexed by citrate.

Zinc, manganese, and cobalt are not important interferences in small amounts, although cobalt and iron together can cause difficulty. If large amounts are present, they should be removed or the precipitation carried out in weakly acid solution.

Silicon and tungsten in small amounts do not interfere. Gold, platinum and palladium are stated to interfere, but are not commonly found.

APPARATUS

Beakers, Griffin low form:	250 ml, 400 ml.
Funnels, Bunsen filtering, long stem:	75 mm dia.
Beakers, electrolytic:	300 ml.
Electrodeposition apparatus:	for description see METHOD Cu-1.
Platinum gauze anodes:	
Platinum spiral cathodes:	
Crucibles, fritted glass, high form:	med. porosity, 50 ml size.
Flask, filtering, with tubulature:	
Crucible adapter for filtering flask:	

REAGENTS

Hydrochloric acid:	
Hydrochloric acid, dil:	1:1 (v/v).
Hydrobromic acid:	
Nitric acid:	
Sulphuric acid, dil:	1:1 (v/v).
Sulphuric acid wash solution:	1% (v/v).
Ammonium hydroxide:	
Sodium carbonate:	
Hydrogen sulphide:	cylinder or lecture bottle.
Hydrogen sulphide wash solution:	1% (v/v) hydrochloric acid solution saturated with hydrogen sulphide.
Bromine water:	water saturated with bromine.
Ammonium chloride:	
Sodium citrate:	
Dimethyl glyoxime solution:	1 gm in 100 ml of ethyl alcohol.
Litmus or pHydrion papers:	

PROCEDURE

A. Preliminary Treatment

1. *Solid Samples*

Weigh a suitable sample (0.01 to 0.1 gm Ni) into a 250-ml beaker. Add 20 ml diluted hydrochloric acid and 5 ml of hydrobromic acid. Boil for 15 to 20 minutes. Cool, add 5 ml nitric acid and 10 ml diluted sulphuric acid, and evaporate to strong fumes. Cool, wash down the sides of the beaker and heat until most of the

free acid is expelled, but not to complete dryness. Cool, digest with 25-30 ml of water until the soluble salts are in solution. Filter through a retentive filter paper into a 400-ml beaker, using filter pulp if necessary. Wash the residue with hot sulphuric acid wash solution. If there is a possibility that the residue contains nickel, fuse with six times its weight of sodium carbonate in a porcelain crucible and digest the cooled melt with hydrochloric acid. Add 5 ml of diluted sulphuric acid and take to fumes to dehydrate silica. Dilute to about 50 ml with water. Filter and add the filtrate to the main body of solution.

2. *Solution Samples*

Pipette a suitable aliquot into a 400-ml beaker, dilute to 100 ml and neutralize with nitric acid if basic.

B. Removal of Interfering Ions

1. *Electrolytic Method*

This step can be omitted if copper is known to be absent.

Transfer the solution to a 300-ml electrolytic beaker and dilute to 100-150 ml. Neutralize. Add 2 ml of nitric acid. Place the beaker in the electrodeposition apparatus. Insert the electrodes and deposit the copper for 15-20 minutes at 4 volts, 1 amp. Raise and wash the electrodes while the current is still running. Transfer the solution to a 400-ml beaker.

2. *Hydrogen Sulphide Method*

Dilute the solution from Section A to about 150 ml. Add ammonium hydroxide dropwise until the precipitate which forms re-dissolves slowly (i.e. until a slight permanent precipitate is obtained). Clear with a few drops of hydrochloric acid. Add 1 gm of sodium sulphite, and boil to expel any excess SO_2. Add 5-7 ml of concentrated hydrochloric acid and pass hydrogen sulphide until precipitation is complete (about 10 minutes is sufficient). Filter through a No. 32 Whatman paper into a 400-ml beaker and wash the precipitate with hydrogen sulphide wash solution. Boil the filtrate to expel hydrogen sulphide.

C. Precipitation of Nickel

Dilute the solutions from Section B (1) or B (2) to about 200 ml. Add 5-10 ml of bromine water, cover the beaker and boil 5-10 minutes, finally removing the cover and boiling to expel all the bromine. Filter if not perfectly clear. Add 1-2 gm of ammonium chloride (more if the zinc content is high). Add 3-8 gm of sodium citrate, depending on the amount of iron present. Add a slight excess of ammonium hydroxide. Make just acid to litmus with hydrochloric acid and add a few drops in excess.

Heat to 60-80°C, and add 5 ml of dimethyl glyoxime solution for each 0.01 gm of nickel present (not more than 10 ml if the nickel content is low). Stir and add ammonium hydroxide dropwise until the solution is alkaline to litmus. Add 2 ml of ammonium hydroxide in excess. Stir well and set aside in a warm place for 30 minutes, or for 12 hours if the precipitate is not heavy.

Filter through a tared, sintered glass filtering crucible (medium porosity). Wash the precipitate with cold water. Dry for 1 hour at 110-120°C, cool in a desiccator and weigh. Record the weight, subtract the tare of the crucible and record the precipitate weight.

CALCULATIONS

$$\% \text{ Ni} = \frac{\text{wt. ppt.} \times 0.2031}{\text{sample weight}} \times 100$$

$$\text{gm/l Ni} = \frac{\text{wt. ppt.} \times 0.2031}{\text{sample volume}} \times 1000$$

If no precipitate is obtained report the sample as containing "less than" the minimum amount, based on the sample weight or volume used, rather than using the term "not detected". The minimum weight detectable can be taken as 1 mg and the result reported on this basis, i.e.

$$\% \text{ Ni} = \text{less than } \frac{0.001}{\text{wt. sample}} \times 100$$

References

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The Colorimetric Determination of Nickel with Dimethyl Glyoxime

METHOD Ni-2

SCOPE

This method is intended primarily for the determination of traces of nickel in ores, solutions and mill products. Nickel is not a common constituent of uranium ores from the major producing areas (except Great Bear Lake) and the principal application of the method is for the detection of attack on stainless steel (e.g. agitator mechanisms) during the leaching process. It is necessary, of course, to determine first that any nickel detected in the leach liquor is not derived from the ore.

Another application that has been suggested, is concerned with the use of nickel as a chemical tracer, added to solutions to follow their courses through the mill. The presence of the radioactive elements uranium and thorium, and their decay products, renders the application of radioactive tracer techniques difficult. Nickel as a tracer combines the advantages of reasonable cost with cheap and highly sensitive detection methods, and this consideration is often coupled with the fact that nickel is not encountered naturally in these ores. It may therefore be of value in detecting malfunctioning of valves that can result in losses of uranium or valuable reagents.

RANGE

The procedure as outlined is suitable for the determination of 10 to 100γ of nickel in the final 100-ml volume used for colour development, using spectrophotometer cells with 50-mm light path. In special cases a 25-ml volume can be used for colour development, further reducing the lower limit.

OUTLINE

The method is based on the characteristic red, water-soluble complex of Ni(IV) with dimethyl glyoxime. The colour obtained, and therefore, presumably, the nature of the complex, is dependent on the acidity of the nickel solution. In the procedure usually recommended (1, 2), an oxidizing agent such as bromine, iodine or persulphate (7) is added to a slightly ammoniacal solution before the addition of the dimethyl glyoxime, which gives a reddish brown colour. If, however the oxidizing agent is added to an acid solution, followed by the addition of ammonia and dimethyl glyoxime, a brownish solution is obtained (1). It has been found here that reversing the usual order of addition, that is, addition of the oxidizing agent to an ammoniacal solution *before* the addition of the dimethyl glyoxime, gives more reproducible results and does not require the close control of conditions that is necessary when the solution is oxidized before being made ammoniacal (3).

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The following elements, in the amounts shown, do not interfere with the direct colorimetric determination of nickel: $AgSO_4$, 0.01 gm; ZrO_2, 0.01 gm; La_2O_3, 0.02 gm; Sm_2O_3, 0.01 gm; SnO_2, 0.01 gm; Y_2O_3, 0.01 gm; ThO_2, 0.02 gm; UO_2, 0.04 gm; BiO, 0.02 gm; PbO, 0.02 gm; MoO_3, 0.02 gm; $FeCl_3$, 0.02 gm; TiO_2, 0.02 gm; CuO, 0.01 mg; and CoO, 0.01 mg (3). Bromide, chloride, arsenate, sulphate, phosphate, perchlorate, oxalate, acetate, and the alkali metals do not interfere (1).

The chief interfering elements are the platinum metals, copper, cobalt, manganese, cerium, chromium, and vanadium. The interference of chromium, vanadium and cerium result from the fact that they consume oxidant so that the resulting redox potential is insufficient for the oxidation of all the nickel, leading to low results. This can be substantially overcome by adding a larger excess of oxidant before colour development. For example, up to 0.02 gm each of vanadyl sulphate and ceric sulphate do not interfere significantly if the amount of oxidant added is increased sufficiently to provide for their oxidation and that of nickel (3).

The platinum metals and large amounts of copper are removed by electrodeposition or by precipitation with either hydrogen sulphide or thioacetamide. This precipitation will also eliminate lead, silver, and bismuth (6).

Large amounts of manganese are eliminated by precipitation as manganese dioxide, using nitric acid and potassium chlorate (5).

Nickel (II) can be separated from at least 0.02 gm each of cobalt, cerium, chromium, vanadium, copper, and manganese by extraction from an ammoniacal dimethyl glyoxime solution using chloroform (1, 2, 4). Nickel (IV) dimethyl glyoxime is not extracted with chloroform, so that strong oxidants, such as chlorate, permanganate, cerate etc., must be absent. Chlorate (together with iodate, bromine and iodine if present) is removed during dissolution of the sample.

Permanganate and cerate are reduced with hydrogen peroxide (3), instead of hydroxylamine hydrochloride as usually recommended (4). This has the advantage that ferric iron is not reduced and hence does not use up dimethyl glyoxime. Furthermore, the excess oxidant is easily expelled by boiling. Such elements as iron, uranium, titanium and aluminum are kept in solution at the high pH by complexing them with citrate or tartrate. Copper, cobalt and a few other elements form complexes with dimethyl glyoxime which are partially extracted by chloroform. Cobalt and copper are removed from the chloroform layer by back-washing it with weak ammonium hydroxide. Two such washes are usually sufficient to remove cobalt, but the presence of large amounts of copper will necessitate five or six washes, and its prior removal by electrodeposition or sulphate precipitation (as described above) is therefore recommended.

After the weak ammonia scrub treatment, nickel is stripped from the chloroform layer using a weak solution of hydrochloric acid, and the nickel (IV) dimethyl glyoxime colour is developed and read.

Dissolution of the sample is usually accomplished with nitric acid, potassium chlorate and hydrochloric acid, this treatment being particularly useful for opening the sulphidic minerals with which nickel is usually associated. A fusion with potassium pyrosulphate then effectively breaks up the more refractory minerals which resist the initial attack.

In some cases, more rapid and effective decomposition can be achieved using hydrochloric and hydrobromic acids for the initial attack, followed by a sodium carbonate fusion of the insoluble residue (5, 6).

APPARATUS

Beakers, Griffin, low form:	250 and 400 ml sizes
Filter paper:	Whatman Nos. 30 and 42
Crucibles, Coors, porcelain:	30 or 40 ml sizes
Hot plate:	
Crucible tongs:	stainless steel
Meker gas burner:	
Tripod:	
Triangles:	silica covered
Flasks, volumetric:	100, 250 and 500 ml sizes
Funnels, Bunsen filtering, long-stem, fluted:	65 mm diameter
Funnel support stand:	
Spectrophotometer, Beckman:	Model B, or equivalent
Electrodeposition apparatus:	*see* METHOD Cu-1
Platinum electrodes:	for electrodeposition apparatus
Pipettes, volumetric:	1, 2, 3, 5, 10, 25 and 50 ml
Beaker tongs:	
Wash bottles:	1000 ml size
Dropping bottles:	
Separatory funnels:	250 ml size, preferably with Teflon stopcocks
Separatory funnel stand:	
Graduated cylinders:	5, 10, 15 and 25 ml sizes
Reagent bottles:	
Crucibles, platinum:	25 or 30 ml size
Crucible tongs:	platinum-tipped

REAGENTS

Chloroform:	
Bromine water, saturated:	
Iodine solution, 0.1 N:	the volumetric standard solution can be used
Dimethyl glyoxime, 1% alcoholic:	
Hydrogen peroxide, 3%:	1 part of 30% H_2O_2, 9 parts of water
Hydrogen sulphide gas:	Cylinder or Kipp generator
Sodium citrate solution, 10%:	
Ammonium citrate solution, 20%, ammoniacal:	Dissolve 200 gm of citric acid in 1 litre of 1:1 ammonium hydroxide
Citric acid:	
Tartaric acid:	

Hydrobromic acid:	
Hydrochloric acid, 4%:	40 ml of concentrated hydrochloric acid made to 1 litre
Ammonium hydroxide:	
Ammonium hydroxide, 1:1:	
Ammonium hydroxide, 2%:	20 ml of concentrated ammonium hydroxide to 1 litre
Sulphuric acid, 1:1:	
Nitric acid:	
Perchloric acid:	
Sodium carbonate:	
Potassium pyrosulphate:	
Potassium chlorate:	
Thioacetamide:	
Thioacetamide, 1% aqueous:	
Standard nickel solution, 1 mg Ni/ml:	Digest 1.000 gm of pure nickel wire or an equivalent amount of a pure nickel salt in nitric and hydrochloric acid until it is completely dissolved, and evaporate the solution to dryness. Dissolve the residue in 20 ml of hydrochloric acid and make to 1 litre. If a salt was used to prepare the solution, standardize the solution gravimetrically by METHOD Ni-1.
Weak standard nickel solution, 5 mg/l:	Dilute 5 ml of the above solution to 1 litre.

Preparation of the Standard Photometric Curve

Transfer aliquots of the weak nickel solution covering range 10 to 500γ of nickel, and a blank, to 100-ml volumetric flasks. Add 4 ml of 1:1 hydrochloric acid, and 5 ml of ammonium citrate solution. Mix and add 5 ml of 1:1 ammonium hydroxide solution. Dilute to 30-40 ml with water, and add 18-20 drops of bromine water (or 1 ml of 0.1 N. iodine solution). Swirl, add 3 ml of 1% alcoholic dimethyl glyoxime solution and swirl again. Dilute to the mark, mix well and let stand 5 minutes. Read on the spectrophotometer at 530 mμ, using 1-cm and 5-cm cells against the reagent blank. Plot a curve of optical density against γ of nickel in 100 ml.

PROCEDURE

A. Preliminary Treatment

Ores and Precipitates

Transfer a weighed portion of the sample (0.01 to 25 mg Ni) to a 250-ml beaker. For samples with very low nickel contents, weigh out duplicate samples. Add 30 ml of nitric acid, cover and let stand 10 minutes. Boil until red fumes are no longer evolved and then carefully add potassium chlorate a little at a time until decomposition is complete. Wash down the sides of the beaker, add 15 ml of hydrochloric acid and evaporate to dryness to dehydrate the silica. Digest the residue in 10 ml of hydrochloric acid and 30 ml of distilled water to dissolve the soluble salts. Filter through a No. 30 Whatman filter paper into a clean beaker. Wash the paper and residue a few times with hot water and reserve the filtrate and washings.

Put the filter paper and its contents into a porcelain crucible and dry, char, and ignite it. Fuse the residue with 3 gm of potassium pyrosulphate. Transfer the cooled melt to the original beaker and digest it in 10 ml of hydrochloric acid

and 30 ml of distilled water. Filter through a No. 30 or No. 42 Whatman filter paper into the beaker containing the reserved filtrates. Wash the paper and residue with hot water, receiving the washings in the same beaker, and discard the residue. Evaporate the combined filtrates and washings to dryness.

Solutions—Organic Materials Absent

Pipette a suitable volume (0.01 to 25 mg Ni) of the sample into a 250-ml beaker, add 10 ml of hydrochloric acid and evaporate to dryness. Measure out duplicate samples for material of low nickel content.

Solutions—Organic Materials Present

Pipette a suitable volume (0.01 to 25 mg Ni) of the solution into a 250-ml beaker (duplicates if the nickel content is low). Add 15 ml of nitric acid and evaporate to small volume. Add an additional 10 ml of nitric acid and 5 ml of perchloric acid. Evaporate to strong fumes of perchloric acid. Add 4 ml of dilute sulphuric acid (1:1) and evaporate to dryness.

B. Arsenic Removal (omit if arsenic absent)

Take up the dried residue with 20 ml of hydrochloric acid, 10 ml of hydrobromic acid and 5 ml of dilute sulphuric acid (1:1). Evaporate to dryness and fume to expel arsenic. If much arsenic is present, add 15 ml of hydrochloric acid, 3 ml of dilute sulphuric acid (1:1), and 10 ml of hydrobromic acid. Evaporate to dryness and fume as before.

C. Manganese Removal (omit if less than 0.01 gm Mn will be present in the aliquot taken for colour development)

Digest the residue with 15 ml of nitric acid and add potassium chlorate in small portions until no more manganese dioxide precipitates. Dilute to 30 ml with distilled water, warm and filter through a Whatman No. 30 filter paper into a clean beaker. Wash the residue with hot water and discard it. To the filtrate, add 5-6 ml of dilute sulphuric acid (1:1) and evaporate it to dryness.

D. Copper Removal (omit if the copper content is low)

Electrodeposition

Digest the residue (from the preliminary treatment, or from the arsenic or manganese separations above) with a mixture containing 5 ml of dilute sulphuric acid (1:1), 1 ml of nitric acid and 30 ml of water. When all the soluble material has dissolved, cool, dilute to 100 ml and electroplate the copper on the electrodeposition apparatus for about 1 hour at 1.5 to 2 amperes. Raise and wash the electrodes into the beaker while the current is still turned on. Remove the beaker from the apparatus and evaporate the solution to dryness.

Hydrogen Sulphide (or Thioacetamide) Precipitation

1. Alternatively, take up the residue from the prior treatment with 5 ml of hydrochloric acid and 60 ml of water. Add 2 gm of sodium sulphite, then boil until the excess sulphur dioxide is expelled.

If hydrogen sulphide is to be used for the precipitation, pass the gas through the solution for 15 minutes, dilute to 100 ml with hot water, and continue gassing for 10 minutes more. Filter through a Whatman No. 30 (or 42) filter paper and wash the paper with warm acidulated hydrogen sulphide solution. Reserve the filtrate.

2. If thioacetamide is to be used as the precipitating agent, take the solution after expulsion of sulphur dioxide and add 25 ml of a freshly prepared solution of 1% thioacetamide. Dilute to 100 ml and digest at 80°C for 20 minutes. Add 10 ml more of the thioacetamide solution and continue heating for an additional 10 minutes. Filter and wash the precipitate with a warm acidulated 0.1% thioacetamide solution. Reserve the filtrate.

If the volume of precipitate from either of the above separations is large, rinse most of it back into the original beaker, place the beaker under the funnel and dissolve any precipitate remaining on the paper with a mixture of nitric acid and bromine water, finally washing the paper with water. Transfer the beaker to a hot plate, add 4 ml of dilute sulphuric acid (1:1) and evaporate to dryness. Dissolve the residue in hydrochloric acid, dilute with water, and reprecipitate the Group II elements as before. Filter into the beaker containing the reserved filtrate. Wash the paper and precipitate as before and discard the precipitate (unless copper or bismuth is to be determined on the same sample).

Boil the filtrate until all the hydrogen sulphide is expelled. Add 2 ml of 3% hydrogen peroxide, boil and evaporate the solution just to dryness.

E. Extraction of Nickelous Dimethyl Glyoxime from Ammonical Citrate Solution

Digest the residue with 6 ml of dilute hydrochloric acid (1:1) and 30 ml of distilled water. Add 10 drops of 3% hydrogen peroxide to oxidize any reduced iron and reduce any manganese or cerium that may still be present.

Boil the solution until all excess peroxide is expelled and transfer to a 250-ml separatory funnel. Rinse the beaker with two 5-ml portions of water, adding the rinsings to the funnel. Add 5 ml of a 10% solution of sodium citrate or citric acid and then make alkaline to litmus by dropwise addition of dilute ammonium hydroxide (1:1). Add 10 drops in excess, followed by 20 ml of a 1% alcoholic solution of dimethyl glyoxime. Shake and let stand for 10 minutes. Add 15 ml of chloroform to the funnel and shake for 2 minutes. Let the phases separate and run the chloroform into a clean separatory funnel. Repeat the chloroform extraction twice more using 15 ml each time. Discard the aqueous layer.

If the chloroform extract (which should be pale yellow or colourless) is coloured blue, pink, or brown, then copper, manganese or cobalt has probably been extracted. In this case, add 15 ml of 2% ammonium hydroxide solution to the combined chloroform extracts. Shake for 2 minutes and let the phases separate. Run the chloroform extract into a clean separatory funnel. Repeat the washing procedure using 2% ammonium hydroxide until the chloroform extract is colourless or pale yellow. As a rule, two washings are sufficient (unless copper is present). Reserve both the aqueous and chloroform layers.

Scrub the combined ammonia wash solutions with 10 ml of chloroform and add this to the washed chloroform extract, discarding the scrubbed ammonia washings.

To the funnel containing the combined chloroform extract, add 20 ml of 4% hydrochloric acid. Shake for 2 minutes, let the phases separate and run the chloroform into a clean separatory funnel. Repeat the acid stripping twice more using 10 ml of 4% acid each time. (The stripped chloroform can be re-used.)

Colour Development

In the case of the residues from sections, A, B, C, and D above, add 10 ml of dilute hydrochloric acid (1:1), 10 ml of water, and 8 to 10 drops of 3% hydrogen peroxide. Boil until all the excess hydrogen peroxide is expelled.

In the case of the strippings from section E, this treatment is not required.

In either case, transfer the solution to a 100-ml volumetric flask. Pipette duplicate aliquots (containing 10 to 500γ Ni), one to each of two 100-ml volumetric flasks, and dilute to about 50 ml.

In the case of samples with very low nickel contents, duplicates will have been carried through the whole procedure. Transfer each to a separate 100-ml (or smaller) volumetric flask. If smaller flasks are used, reduce the volumes of the reagents added proportionately. To both flasks, add 5 ml of dilute ammonium citrate solution and 5 ml of dilute ammonium hydroxide, and swirl to mix. Add 20 drops of bromine water and mix again. Finally, add 3 ml of 1% dimethyl glyoxime, to *one* flask only. Dilute both flasks to the mark and mix well. Let stand 5 minutes. Read the optical density of the sample solution containing dimethyl glyoxime against the other sample solution as a blank, at 530 mμ, in the Beckman Model B spectrophotometer. Use 1-cm cells initially, and if the absorbance is less than 0.200 repeat the reading using 5-cm cells. Record the reading, and read and record the corresponding nickel content from the appropriate calibration graph depending on final volume and cell path employed.

CALCULATIONS

Solids

$$\% \text{ Ni} = \frac{\gamma \text{ Ni (from graph)}}{1{,}000{,}000} \times \frac{\text{dilution factor}}{\text{sample weight}} \times 100$$

Solutions

$$\text{gm/l} = \frac{\gamma \text{ Ni (from graph)}}{1{,}000{,}000} \times \frac{\text{dilution factor}}{\text{sample volume}} \times 1000$$

If no nickel is detected, report the assay as "less than" the limit of detection, an actual figure based on the sample weights and volumes used.

References

1. Sandell, E. B.: Colorimetric Determination of Traces of Metals, 2nd ed., New York, Interscience Pub., Inc., 1950.
2. Welcher, F. J.: Organic Analytical Reagents, vol. III, New York, D. Van Nostrand Co. Inc., 1947.
3. Roloson, F. P.: Radioactivity Div., *Mines Branch, Ottawa*, 1958.
4. ASTM Methods of Chemical Analysis of Metals, Philadelphia, American Society for Testing Materials, 1950.
5. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I.: Applied Inorganic Analysis, 2nd ed., New York, John Wiley and Sons, 1953.
6. Furman, N. H., Ed.: Scott's Standard Methods of Chemical Analysis. vol. 1, 5th ed., New York, D. Van Nostrand Co., Inc., 1939.
7. Rodden, C. J., and Petretic, G. J.: Report A-1032, 1944.

The Colorimetric Determination of Nitrate in Mill Products and Solutions

METHOD NO_3-1

SCOPE

The method is applicable to most mill solutions which are low in nitrites. It can be adapted to mill products containing water-soluble nitrates.

RANGE

From 0.01 to 50 gm of nitrate per litre can be determined with an error of less than 5%.

OUTLINE

α-phenoldisulphonic acid forms a bright yellow colour with nitrates in alkaline solution. The colour is stable for at least 24 hours and can be read on a filter photometer or spectrophotometer at about 420 mμ. Nitrites interfere if present in excess of 0.001 gm per litre. They should be converted to nitrates by heating with repeated additions of a few drops of hydrogen peroxide (nitrate-free) and a correction applied for the nitrates so formed. Chlorides if present in excess of 0.1 gm per litre should be removed with silver sulphate. This procedure also removes iodides and bromides. If chlorides are removed with silver sulphate it is better to use an excess of 1:1 ammonium hydroxide for the final colour development, since a slight excess of silver sulphate will result in a dirty precipitate when potassium hydroxide is used, whereas the use of ammonia has no effect. On the other hand ammonium hydroxide does not precipitate copper and nickel (1), (2), (3).

APPARATUS

Photoelectric colorimeter or spectrophotometer:

1 cm. cells or equivalent:

REAGENTS

Phenoldisulphonic acid: Dissolve 25 gm of pure white phenol in 150 ml of pure concentrated sulphuric acid. Add 75 ml of fuming sulphuric acid, (13-15% SO_3), stir well and heat for two hours at 100° C. Two millilitres of this reagent is sufficient for 10 mg of nitrate nitrogen.

Standard nitrate solution: Dissolve 0.72 gm of pure potassium nitrate in 1 litre of water. Evaporate 10 ml of this solution just to dryness on a water bath. Moisten the residue with 2 ml of the phenoldisulphonic acid and dilute to 1 litre. One ml of this solution equals 0.001 mg of nitrate nitrogen or 0.004427 mg of NO_3.

Aluminum hydroxide:	Dissolve pure aluminum foil in acids. Evaporate twice to heavy fumes with sulphuric acid and precipitate the aluminum with a slight excess of ammonium hydroxide. Wash the precipitate thoroughly.
Silver sulphate solution:	Dissolve 4.4 gm of nitrate-free silver sulphate in 1 litre of distilled water.
Potassium hydroxide:	10-12N—Approximately 10 ml will neutralize 2 ml of the sulphonic reagent.
Hydrogen peroxide:	3%.
Sulphuric acid:	
Ammonium hydroxide:	1:1.

PROCEDURE

For Solids

Digest a weighed amount of the solid with distilled water. Filter into a volumetric flask, wash the residue with hot water, cool and dilute to the mark. Pipette an aliquot into a clean beaker and proceed as for solutions.

For Solutions

Carry a blank determination through the procedure.

Pipette an aliquot portion of the solution containing 0.01 to 0.05 mg of nitrate nitrogen into a clean 100-ml beaker and dilute slightly. Add 0.1N H_2SO_4 or KOH until the solution is just slightly alkaline. Add enough silver sulphate to precipitate all but about 0.5 mg of the chlorides as previously determined in a separate sample. Heat the solution to boiling, add a little aluminum hydroxide and then add hydrogen peroxide a few drops at a time to oxidize any nitrites. Boil off the excess peroxide, filter or centrifuge, and wash the precipitate thoroughly with small amounts of water. Discard the precipitate. Add one drop of 6N potassium hydroxide and evaporate the filtrate just to dryness on a steam bath. Add 2 ml of the phenoldisulphonic acid and warm gently. Dilute with a little water and cautiously add 12N potassium hydroxide until the full colour is developed plus 2 ml excess. Transfer to a 100-ml volumetric flask and dilute to 100 ml with distilled water. Read the transmittancy on the photoelectric colorimeter at 410 mμ. Determine the amount of nitrate nitrogen in the blank.

CALCULATIONS

By means of a graph in which transmittancy has been plotted against mg NO_3 in 100 ml volume, using standards, determine the nitrate content of the solution and correct for the nitrate in the blank.

Solution Samples

$$\text{gm/l } NO_3 \text{ (as } NO_3) = \frac{\text{mg } NO_3/100 \text{ ml (graph)}}{1000} \times \frac{\text{dil'n}}{\text{aliq. taken}} \times \frac{1000}{\text{sample vol.}}$$

Solid Samples

$$\%\ NO_3 \text{ (as } NO_3) = \frac{\text{mg } NO_3/100 \text{ ml (graph)}}{1000} \times \frac{\text{dil'n}}{\text{aliq. taken}} \times \frac{100}{\text{sample wt.}}$$

If the sample gives approximately the same reading as the reference solution, the amount of NO_3 shall be reported as "less than" the minimum amount detectable (an actual figure based on the sample weight and volumes used). The

minimum amount detectable may be taken as 0.02 mg per 100 ml and the figure to report may be calculated on this basis; for example:

$$\text{gm/l } NO_3 = \text{less than } 0.02 \times \frac{\text{final sol'n vol.}}{\text{aliquot taken}} \times \frac{1000}{\text{sample vol. taken}}$$

References

1. Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I.: Applied Inorganic Analysis, 2nd ed., New York, John Wiley and Sons, 1953.
2. Furman, N. H., Ed.: Scott's Standard Methods of Chemical Analysis, 5th ed., Vol. 2, New York, D. Van Nostrand Co., 1938.
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The Volumetric Determination of Nitrate in Barren Eluates and Strip Solutions

METHOD NO_3-2

SCOPE

The method is suitable for the rapid determination of nitrate for mill control purposes. It is intended to be carried out by operating personnel.

RANGE

The method can be used down to 0.3 gm/l NO_3 (0.005 N NO_3), but is primarily intended for use in the range 0.5 to 1.0 N.

OUTLINE

The nitrate-containing solution is boiled in an acid solution with an excess of ferrous iron, which it oxidizes to the ferric state,

$$NO_3^- + 3\ Fe^{++} + 4H^+ \longrightarrow NO + 3\ Fe^{+++} + 2H_2O$$

The excess ferrous iron is then back-titrated with potassium dichromate using sodium diphenylamine sulphonate indicator in a phosphoric acid-sulphuric acid medium:

$$6\ Fe^{++} + Cr_2O_7 + 14H^+ \longrightarrow Fe^{+++} + 2\ Cr^{+++} + 7H_2O$$

Since ferrous iron is easily air-oxidized when hot, sodium carbonate is added to provide an inert atmosphere during the boiling period (1).

The method is not of general application, but can be applied in certain cases to eluate solutions by titrating a separate portion of the solution with the dichromate and subtracting the titration from that of the excess of ferrous iron to correct for the reducing power of the solution.

APPARATUS

Flasks, Erlenmeyer:	300 ml size.
Watch glasses:	small, to cover mouth of flask (or Tuttle flask covers, size B).
Tripod:	
Wire gauze:	asbestos centre.
Gas burner:	
Flask tongs:	
Burette:	50 ml size.
Pipettes:	1, 5, 10, 25 ml sizes.

REAGENTS

Standard potassium dichromate solution, N/10:	Weigh out 4.904 grams dried $K_2Cr_2O_7$, dissolve in water and dilute to 1 litre in a volumetric flask.
Diphenylamine indicator:	Dissolve 1.6 gm of barium diphenylamine sulphonate in 500 ml of water containing 5 ml concentrated sulphuric acid. Let the barium sulphate formed settle out and decant or filter off the supernatant liquid.
Standard potassium nitrate solution 0.1M:	Dissolve 10.1 gm KNO_3 and dilute to 1 litre with water.
Sodium carbonate:	
Sodium bicarbonate solution, saturated:	
Standard ferrous ammonium sulphate solution, 0.2N:	Dissolve 78.4 gm $Fe(NH_4)_2(SO_4)_2\ 6H_2O$ in 500 ml of water, add 50 ml concentrated sulphuric acid and cool. Filter through a rapid filter paper into a 1 litre volumetric flask, dilute to the mark, and store in a dark bottle.
Sulphuric acid 1:1, v/v:	
Hydrochloric acid, concentrated:	
Phosphoric acid, 85%:	

PROCEDURE

Pipette a suitable aliquot of the solution (2 ml for 0.5 M nitrate solution) into a 300-ml Erlenmeyer flask. Take a second empty Erlenmeyer flask for a blank determination. Add 30 ml concentrated hydrochloric acid, 10 ml diluted sulphuric acid (1:1 v/v), 1 gm of sodium carbonate and finally, 25 ml 0.2N ferrous ammonium sulphate solution, to each. Swirl to mix, cover with a watch glass (or Tuttle flask cover) and place on a wire gauze (asbestos centre) on a tripod. Boil the contents of the flask over a low flame until the colour is a light reddish brown (about 10 minutes).

Remove from the flame, add about 150 ml saturated sodium bicarbonate (*cautiously*), and cool to room temperature in a stream of cold water.

Add 10 ml dilute sulphuric acid, 5 ml of phosphoric acid and 6 drops of diphenylamine sulphonate indicator.

Titrate the excess ferrous iron in both sample and blank with N/10 potassium dichromate, to a purple end-point. Record the titration, and calculate the nitrate content of the solution.

If the solution contains reducing ions, pipette a second aliquot of the same size as the first into a 300-ml Erlenmeyer flask. Dilute to about 100 ml with water. Add 10 ml 1:1 sulphuric acid, 5 ml phosphoric acid and 6 drops of diphenylamine sulphonate. Titrate with the same N/10 potassium dichromate solution to a purple end-point, and subtract this titration from that of the sample that was boiled, as a correction.

Check the normality of the standard dichromate from time to time by carrying a 10-ml aliquot of standard potassium nitrate solution through the procedure.

CALCULATION

$$\text{Molarity of nitrate solution} = (T_b - T_a) \times \frac{N_a}{3} \times \frac{1}{\text{aliquot taken, ml}}$$

or

$$\text{gm/l } NO_3 = (T_b - T_a) \times N_a \times \frac{62}{3} \times \frac{1}{\text{aliquot taken}}$$

where T_b = Dichromate titration of ferrous ammonium sulphate in blank.

T_a = Dichromate titration of excess ferrous iron in sample solution (corrected if necessary).

N_a = Normality of potassium dichromate solution.

Reference

1. Snell, F. D., and Biffen, F. M.: Commercial Methods of Analysis, p. 153, New York, McGraw-Hill Book Co., Inc., 1944.

The Determination of the Neutralizing Power of Feed Materials and Neutralizing Agents

METHOD N.P.-1

SCOPE

This procedure is intended to provide a rough guide to the amount of acid that will be consumed in acid leaching various materials, and also as an indication of the efficiency of certain materials such as limestone, dolomite, etc., as neutralizing agents for acid solutions. The method is particularly intended for comparing the neutralizing power of cheap neutralizers that are locally available for barren solution neutralization. It does not replace standard leach tests. Results are expressed as milliequivalents of neutralizing power per dry gram.

RANGE

The range covered is 0.01 milliequivalents of neutralizing power per dry gram and up.

OUTLINE

The procedure consists of treating the material with an excess of a standard acid solution and back-titrating the excess with standard caustic solution to determine the amount of acid consumed. If the material contains elements which will produce hydrolytic precipitates and as a result gives an indefinite end-point in the back-titration, the free acid procedure (METHOD F.A.-1) is used for this part of the method. Results are reported as "milliequivalents acid consumed per dry gram of sample" since the purpose to which the result is to be put cannot always be ascertained.

PROCEDURE

Weigh out a suitable sample, containing about 3 to 4 milliequivalents of neutralizing power into a 250-ml beaker, (e.g. for a sample having a neutralizing power of 10 meq. per dry gram, take the equivalent of 0.4 dry grams). A preliminary direct titration using methyl orange as indicator may be necessary to establish the proper sample size, or it may be necessary to try several different sample sizes. The proper sample size will leave an excess of about 10-20 ml of N/10 acid when 50 ml of this acid is added to the sample. If the sample is received as a paste, weigh out a sample for a moisture determination at the same time (*see* METHOD M-1).

To the beaker containing the sample, add 50 ml of N/10 hydrochloric acid, (unless some other acid is specified). Warm to dissolve (do not boil), then let stand for 1 hour. Filter, if necessary and complete the determination on the filtrate by the free acid procedure, METHOD F.A.-1, using the Precision Dow Recordomatic Titrator, i.e. add 25 ml of 28% potassium oxalate solution and

titrate with standard KOH solution. If a precipitate forms before the end-point is reached, repeat the determination using more of the oxalate solution. Record the titration. If elements forming hydrolytic precipitates are known to be absent, the back-titration can be carried out directly using methyl orange indicator.

CALCULATIONS

$$\text{Neutralizing Power, meq/dry gram} = \frac{(T_a N_a - T_b N_b) \times 1000}{W}$$

T_a = Volume of standard acid taken

N_a = Normality of standard acid taken

T_b = Volume of standard base used

N_b = Normality of standard base used

W = Dry weight of sample, grams.

If the sample titration is approximately equivalent to the amount of acid added, the result shall be reported as less than the minimum amount detectable (an actual figure based on the sample weight taken). The minimum amount detectable is 0.1 milliequivalent, and the figure to report may be calculated on this basis, i.e.

$$\text{Neutralizing Power (meq/dry gram)} = \text{less than } \frac{0.1}{W}$$

Determination of Phosphorus by the Alkalimetric Molybdate Method

METHOD P-1

SCOPE

The volumetric method is preferred for the determination of phosphorus in the higher ranges since it does not require the same attention to detail as does the colorimetric method, and is not as dependent on absolute absence of traces of contamination in the equipment used. As described here, it is intended for use on phosphate concentrates, for uranous phosphate precipitates, and for leach liquors high in phosphorus.

RANGE

The assay sample should contain 5 to 50 mg P_2O_5, so that 0.1% or 0.1 gm/l represents the lower limit of the method. The maximum error is of the order of 2%.

OUTLINE

Phosphorus, (as orthophosphate only) can be precipitated from nitric acid medium as ammonium phosphomolybdate, by means of ammonium molybdate in an ammonium nitrate-nitric acid solution.

$$H_3PO_4 + 12\,(NH_4)_2\,MoO_4 + 23\,HNO_3 \rightleftharpoons (NH_4)_3\,PO_4.\,12\,MoO_3.\,2HNO_3.\,H_2O + 21\,NH_4NO_3 + 12\,H_2O$$

The stoichiometry is fairly close to this reaction, although results have a tendency to be low.

The precipitate so obtained is thoroughly washed with dilute potassium nitrate, which converts it to the composition $(NH_4)_3PO_4.12\,MoO_3$. This is then allowed to react with a measured amount of standard sodium hydroxide in excess of the amount required to neutralize it. The excess is back-titrated with standard nitric acid and the amount of sodium hydroxide consumed by the precipitate is calculated.

$$(NH_4)_3\,PO_4.\,12\,MoO_3 + 23\,NaOH \rightleftharpoons 11\,Na_2MoO_4 + (NH_4)_2\,MoO_4 + NaNH_4\,HPO_4 + 11\,H_2O.$$

The method is not new (1), but it remains one of the most popular methods for determining phosphorus (2, 3, 4, 9).

The requirement that the phosphate be present as orthophosphate offers no difficulties since it is seldom present in any other form in ores or in the uranous phosphate precipitate. For precipitation, ammonium molybdate must be present

in excess and a temperature in the range 20°-45° C must be employed. Precipitation occurs more rapidly at the higher temperature, but the use of temperatures above 45° C will lead to contamination from arsenate, vanadate and silica. Shaking also hastens precipitation. Precipitation may be complete in 10 minutes, but a longer period is preferred and for highest accuracy the solution should stand overnight, especially if retarding compounds such as vanadate, are present.

Sulphates, chlorides and fluorides, retard precipitation and should not be present in large amounts. As much as 10% hydrochloric acid or 5% sulphuric acid (by volume), may be present if more ammonium nitrate and molybdate reagent are added, and if a longer precipitation time is allowed. As much as 5% of hydrofluoric acid may be present if it is converted to fluoboric acid. It is best removed if much is present. Moderate amounts of perchloric acid are without effect.

Copper, nickel and hexavalent chromium should be removed if present in significant amounts. An ammonia separation using iron as a collector for phosphate, can be used. Alternatively H_2S or caustic separations may be used. These do not precipitate phosphate.

Arsenic and silicon retard precipitation and also are precipitated by a similar mechanism to that of phosphorus. At 20° to 25° C, moderate amounts will not precipitate. Arsenic can be volatilized by fuming the sample with hydrochloric and hydrobromic acids. Silica can be either dehydrated and filtered off, or volatilized with nitric and hydrofluoric acids.

Tungsten also precipitates with the reagent and must be absent. If its presence is suspected it should be removed by digesting with nitric and hydrochloric acids and filtering. The residue so obtained must be treated separately to recover the phosphate it contains.

Titanium and zirconium, as well as thorium, niobium, tantalum and tin, may cause the loss of phosphorus in the preliminary operations unless the insoluble residues are fused with sodium carbonate and the phosphate extracted with water (9).

If selenium and tellurium are present, this method cannot be used. Their presence in uranium ores is not common.

Vanadium, particularly in the quinquevalent form, tends to precipitate with phosphorus. For this reason, ferrous sulphate followed by a few drops of sulphurous acid, is added to reduce V(V) (2, 4). If the solution does not contain iron, ferric nitrate is then added to prevent subsequent reduction of the molybdenum. Quadrivalent vanadium retards precipitation, but is not carried down by ammonium phosphomolybdate if the precipitation is carried out at 10° to 20° C (5). Since vanadium is present in many Canadian ores, this procedure employs the lower temperature and longer precipitation time necessary to overcome its interference.

It should be pointed out that the phenolphthalein end-point is actually past the stoichiometric end-point for the titration of molybdic acid by sodium hydroxide. The true end-point occurs at pH 7.5, a pH which can be indicated by a pH meter or a suitable mixed indicator. The use of phenolphthalein gives a result which, stoichiometrically is about 1% high (6). This is overcome in the present method by standardizing the sodium hydroxide against standard phosphate rock, which has the further advantage of correcting for non-stoichiometry of the precipitate itself.

The use of citric or tartaric acid in the molybdate reagent as recommended by Kassner (6) has been briefly investigated in this laboratory and found unreliable

when dealing with materials of widely varying composition. Double strength molybdate reagent was required, and there did not appear to be any corresponding advantages (7).

Perchloric acid, used in this method is a vigorous oxidizing agent when hot. It is to be used only in special fume hoods designated for the purpose, and organic material must not be used in these hoods at any time.

OCCURENCE

Most ores of uranium contain phosphate in the form of the mineral apatite or fluor apatite $(CaF)Ca_4(PO_4)_3$. It occurs in small amounts as the mineral monazite (rare earth orthophosphate), a common accessory mineral in many Canadian pegmatitic deposits and in the ores of the Blind River area, and also as the secondary uranium minerals autunite and torbernite in weathered material derived from these ores.

The phosphate content of ores from Blind River is low ($< .05$). Somewhat larger quantities are found in those from the Bancroft (0.01 to 0.2) and Beaverlodge (0.2 to 0.5) areas.

The only Canadian property with large amounts of phosphate in its ore is the Eldorado mine at Port Radium (approx. 1%).

In the mill, synthetic calcium phosphate is added to precipitate uranium phosphate in the "Aluminum Reduction" process. Uranous and uranyl phosphates may be found in leach residues as the result of poor control of the pH of the leach liquor, if phosphate is present in the ore. Titanium or thorium would also be expected to precipitate as phosphates during leaching.

Phosphate is also found in the uranium concentrate. It is of course a major constituent in the precipitate from the aluminum reduction process. It is a significant impurity in the precipitate from the ion exchange process which tends to concentrate this ion from solutions containing trace quantities, and since its presence is undesirable in the refining process, a specification limiting the amount permitted has been set.

APPARATUS

Beakers, Griffin low form:	250 ml.
Crucibles, platinum, 30 ml:	
Watch-glasses:	
Flasks, Erlenmeyer, 300 ml, with stopper:	
Filter funnels and stands:	
Sintered glass crucibles (optional):	fine or medium porosity, size 25-30 ml.
Funnel, Moore-Shimer (optional):	sim. to Cenco 15195.
Flasks, filtering, with tubulation:	500 ml size.
Filter paper:	Whatman No. 30., Whatman No. 7.

Volumetric flasks:	250, 500 ml.
Pipettes:	10, 25, 50 ml.
Burette:	50 ml.

REAGENTS

Hydrochloric acid concentrated:	
Hydrobromic acid, concentrated:	
Nitric acid, concentrated:	
Perchloric acid, concentrated:	
Sodium carbonate:	CP
Sodium hydroxide solution 10%:	Prepared fresh by diluting reagent 50% sodium hydroxide solution.
Sodium hydroxide solution, 5%:	Add 0.05% sodium sulphate.
Ferrous sulphate solution:	10 gm $FeSO_4 . 7H_2O$ in 100 ml 5% H_2SO_4(w/v).
Sulphurous acid; 6% solution:	
Ferric nitrate; 5% solution:	
Ammonium nitrate:	
Ammonium molybdate solution:	Dissolve 236 gm of molybdic acid (85%) in a solution of 480 ml water and 280 ml NH_4OH. Slowly pour this solution into a solution of 1920 ml water and 920 ml HNO_3, with constant stirring. Let stand overnight and filter into 1 gal. polyethylene bottles. Filter again just before using.
Standard sodium hydroxide solution: (approx. 0.8N)	Dilute 280 ml of C.P. 50% sodium hydroxide solution to 4 litres. Cool and store in a polyethylene bottle. Standardize this solution against a standard phosphate rock sample that has been carried through all the steps of the procedure. Express its strength as "mg P_2O_5 per ml".
Standard phosphate rock:	National Bureau of Standards, Standard Samples Nos. 56a or 120.
Phenolphthalein indicator:	1% in alcohol.
Standard nitric acid solution: (approx. 0.4N)	Dilute 100 ml concentrated nitric acid to 4 litres with water. Standardize against the above sodium hydroxide solution using phenolphthalein indicator. It is convenient to adjust the nitric acid solution to have just half the strength of the sodium hydroxide solution. Express the strength of the acid as "ml NaOH solution equivalent per ml nitric acid solution." This is factor f_2 in the equation given under "Calculations".
Wash solution:	Potassium nitrate solution, 1%.

Standardization of Sodium Hydroxide Solution in Terms of P_2O_5

Weigh out several 1-gram portions of standard phosphate rock (NBS-56a or 120) into a 250-ml beaker. Take into solution as for samples, using the simple acid treatment. Omit the special separations given, and transfer the solution to a 100-ml volumetric flask. Dilute to the mark, mix well, and transfer aliquots, covering the range 5 to 50 mg P_2O_5, to glass-stoppered 300-ml Erlenmeyer flasks. Precipitate the phosphorus, wash, dissolve and titrate by the method given in the following procedure.

From the data so obtained calculate the factor (gm P_2O_5 per ml standard sodium hydroxide solution) referred to as f_1 in the equation given under "Calculations".

$$f_1 = \frac{P_2O_5 \text{ conc } (\%) \text{ of standard} \times \text{wt taken}}{V - f_2 T} \times \frac{\text{aliquot taken}}{\text{final volume}}$$

where V = volume of standard sodium hydroxide used to dissolve the phosphomolybdate precipitate

f_2 = factor for standard nitric acid solution "ml standard sodium hydroxide solution per ml standard nitric acid solution"

T = volume of standard nitric acid solution used to titrate the excess of standard sodium hydroxide solution

NOTE: $f_1 \doteqdot 0.0025$

PROCEDURE

A. Preliminary Treatment

1. *Solid Samples*

Decomposition of Ores—Weigh a suitable portion (Table 1) of the finely ground sample into a 250-ml beaker. Add 10 ml water, 10-15 ml concentrated hydrochloric acid and 5 to 10 ml hydrobromic acid. Cover the beaker and boil for 15 to 20 minutes. Move the cover to one side and let evaporate to small volume, taking care not to bake. Cool, and rinse down the sides with a small amount of water. Cautiously add 5 ml of nitric acid and cover. Let stand till the evolution of bromine subsides. Remove the cover and boil off the bulk of the bromine. Finally add 5 to 10 ml of perchloric acid and heat to strong fumes. Cover the beaker and let reflux 20 to 30 minutes. Cool, wash down the sides of the beaker. Replace on the hot plate and evaporate just to dryness, but do not bake. (If iron is not being determined on an aliquot of the filtrate, this solution need not be taken to dryness.)

Add 30-40 ml water and boil to dissolve soluble salts. Filter through a Whatman No. 30 filter paper, and wash the residue alternately with hot 1% acid and hot water, several times.

Unless it is known that the residue contains no phosphate, transfer the filter paper and contents to a 30-ml platinum crucible. Burn off the paper, mix the residue with approximately five times its weight of sodium carbonate and fuse over a low flame at first, gradually increasing the heat until about 1000° C is reached. Hold this temperature until the mass is quiescent. Cool, extract the melt with hot water, transfer to a 250-ml beaker and digest till the mass disintegrates. Filter through a Whatman No. 30 paper, wash the residue with hot 1% sodium carbonate solution and discard it. To the filtrate, add 5 ml of perchloric acid and take just to dryness to dehydrate the silica. Dissolve the soluble salts in hot water and filter. Combine the filtrate with the filtrate from the acid digestion, transfer to a volumetric flask of suitable size, and dilute to volume.

2. *Solution Samples*

Pipette an aliquot portion into a volumetric flask of suitable size (Table 2), add 5 or 10 ml of nitric acid, and dilute to volume. Alternatively, if much arsenic

is present, pipette the sample into a 250-ml beaker, evaporate to dryness and carry through the acid treatment as for solids.

3. *Organic Phosphate-Kerosene Solution*

Pipette a 20-ml aliquot of the organic phosphate solution into a 150-ml beaker and evaporate off the kerosene on the steam bath. Add about 5 ml of fuming nitric acid, cover the beaker and heat gently for 5-10 minutes. Cool, add 3 ml of concentrated sulphuric acid and 5 ml more of fuming nitric acid. Heat until charring takes place. This occurs suddenly and rather violently, so that it is necessary to keep a close watch on the sample to prevent loss by spattering. Continue heating for a few minutes to permit the charring reaction to continue. Add a further 5 ml of nitric acid and heat until the solution is a light brown. Add 10 ml of a mixture of 2 parts nitric acid and 1 part perchloric acid, and take to fumes of perchloric acid. If the solution is still tinted yellowish or brownish, add a few drops of concentrated nitric acid dropwise to the fuming solution, taking care to keep the beaker covered, and fume again. Continue till the solution is colourless. Cool, dilute with water and continue the balance of the procedure.

B. Separation of Phosphate from Copper, Nickel and Chromium (omit if these elements are absent)

Pipette a suitable aliquot (Tables 1 and 2) into a 250-ml beaker. Adjust the volume to 100-150 ml and add 10 ml of 5% ferric nitrate solution (unless an equivalent amount of iron is already present). Add 2-3 grams of ammonium chloride and 2-3 ml of concentrated hydrochloric acid. Boil and add 2-3 drops of methyl red indicator. Carefully neutralize the hot solution with ammonium hydroxide, stirring vigorously, until the solution turns yellow, then add 1 or 2 ml of concentrated ammonium hydroxide in excess. Boil for 3 minutes more, and filter on a Whatman No. 7 paper. Wash the beaker and precipitate three or four times with a little cool 1% ammonium nitrate solution. Discard the filtrate.

Wash most of the precipitate back into the precipitation beaker with a little water. Place the beaker under the funnel and dissolve any remaining precipitate with a minimum of dilute nitric acid. Dilute to 75-100 ml, add more nitric acid until the precipitate just dissolves, then add 1-2 ml nitric acid in excess.

C. Separation of Iron, Nickel, Cobalt, Titanium, Zirconium or Chromium

Take the solution from the above separation, or, if this step was omitted, pipette a suitable aliquot into a 250-ml beaker and dilute to about 100 ml.

Nearly neutralize with sodium hydroxide solution, heat to boiling, and pour the solution slowly and with constant stirring into 100 ml of a hot fresh 10% solution of sodium hydroxide. Boil for another 2 or 3 minutes, stirring to prevent bumping and let settle. Filter hot on a Whatman No. 30 or 52 paper and wash with hot 5% sodium hydroxide containing a little sodium sulphate. Reserve the filtrate.

Dissolve the precipitate in a minimum of hot dilute nitric acid and repeat the separation. Discard the washed, second precipitate and combine the filtrates.

D. Precipitation of Phosphorus

Transfer the solution, free of interfering ions (except vanadium) into a 300-ml glass-stoppered Erlenmeyer flask and dilute to about 75 ml. Add a few drops of 10% ferric nitrate solution, if the iron content is low, followed by 1-2 gm of ammonium nitrate. Partially neutralize with ammonium hydroxide (i.e. until the slight precipitate formed redissolves slowly). Clear with nitric acid, and add an excess of 5-10 ml of concentrated nitric acid. If vanadium is believed to be

present, cool to 10° C, add sufficient ferrous sulphate solution (about 5 ml) to reduce it, followed by a few drops of 6% sulphurous acid, and if the iron content was low, about 10 ml of the 10% ferric nitrate solution (unless this was added previously).

Cool the solution to room temperature and add the freshly filtered molybdate solution (25 ml plus at least 0.5 ml per mg of P_2O_5 present). If vanadium is known to be present, or if titanium, zirconium, chloride or sulphate have not been removed, the initial amount should be increased to 30 or 40 ml plus 0.5 ml per mg of P_2O_5 present. Stopper the flask, shake vigorously for 1 or 2 minutes and then let stand at room temperature for at least 30 minutes. If vanadium or arsenic are present let the solution stand at least 2 hours, and preferably overnight.

Filter through a retentive filter paper (Whatman No. 7). Wash the flask and precipitate thoroughly with cool 1% potassium nitrate solution. Continue washing until the paper and precipitate are acid-free, as ascertained by testing with blue litmus paper. If large numbers of routine determinations are being made some time can be saved by using Moore-Shimer funnels containing a pad of filter pulp, or sintered glass crucibles of fine or medium porosity, and carrying out the filtration and washing using suction.

A special laboratory layout for this step is shown in reference 8.

Titration of he Phosphomolybdate

Transfer the paper and precipitate to the original 300-ml Erlenmeyer flask, making sure no precipitate is left on the funnel. Dissolve the precipitate by adding a measured amount of the standard sodium hydroxide, calculated to provide 5 to 10 ml in excess. Use either a burette or pipettes, and record the volume added. This volume is referred to as V in the equation given under "Calculations". Shake the flask to ensure complete solution of the yellow precipitate and dilute to about 100 ml.

Add 3 drops of phenolphthalein indicator and titrate with standard nitric acid solution to the disappearance of the pink colour. Record the volume of

Table 1

Dilution Table for Solids, Volumetric Phosphorus Determination

Range %	Sample Weight gm	Dilute to Final Volume ml	Aliquot, take ml
0.1 – 1.0	5	do not dilute	
1 – 5	5*	250	50
	or		
	1.0	do not dilute	
5 – 10	5*	250	25
	or		
	0.5	do not dilute	
10 – 20	5*	500	25
	or		
	0.25	do not dilute	
20 – 50	5*	500	10
	or		
	0.1	do not dilute	

* for non-homogenous samples

Table 2

Dilution Table for Solutions, Volumetric Phosphorus Determination

Range gm/l	Sample Volume ml	Dilute to Final Volume, ml	Aliquot, Take ml
0.1 – 1.0	50	do not dilute	
1 – 5	10	do not dilute	
5 – 10	5	do not dilute	
10 – 20	5	100	50
20 – 50	5	100	25

nitric acid required to titrate the excess sodium hydroxide. This is referred to as T in the equation given under "Calculations".

CALCULATIONS

$$\% P_2O_5 = (V - f_2 T) \times f_1 \times \frac{\text{final volume}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

$$\text{gm/l } P_2O_5 = (V - f_2 T) \times f_1 \times \frac{\text{final volume}}{\text{aliquot taken}} \times \frac{1000}{\text{sample volume}}$$

where V = volume of standard sodium hydroxide solution added to dissolve the phosphomolybdate precipitate

f_2 = factor for standard nitric acid solution, "ml standard sodium hydroxide solution per ml standard nitric acid solution".

T = volume of standard nitric acid solution used to titrate the excess of standard sodium hydroxide solution

f_1 = factor for the standard sodium hydroxide solution "gm P_2O_5 per ml standard sodium hydroxide solution".

If no phosphomolybdate precipitate is obtained the phosphorus content of the sample should be reported as "less than" the minimum amount detectable, an actual value based on the sample weight and dilutions used. This may be taken to be .001 gm P_2O_5 in the aliquot taken and the figure to report can be calculated accordingly, e.g.,

$$\% P_2O_5 = \text{less than } .001 \times \frac{\text{final volume}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

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The Iodometric Determination of Lead as Chromate

METHOD Pb-1

SCOPE

By this procedure, lead may be determined in non-refractory minerals provided that the silver content is negligible.

RANGE

The method can be used for lead in the range 0.10% and up. The sample should not contain more than 0.1 gm lead. The method is *not* recommended for the determination of lead in ores containing less than 0.05%, e.g. it is not satisfactory for determining radiogenic lead in samples containing less than 1% U_3O_8. For such samples, the polarographic method should be used.

OUTLINE

The sample is treated with hydrochloric and nitric acids to decompose sulphides and expel hydrogen sulphide. Evaporation with sulphuric acid dehydrates silica and precipitates lead sulphate which are filtered off.

The lead is dissolved in sodium acetate solution and precipitated as lead chromate by potassium dichromate. The lead chromate and silica are filtered and washed.

The lead chromate is then dissolved in hydrochloric acid, and the chromate ion is determined iodometrically.

APPARATUS

Beakers, Griffin low form, Pyrex:	100 ml, 250 ml sizes.
Flasks, Erlenmeyer:	250 ml.
Funnels, filtering, Bunsen long stem:	
Steam bath:	

REAGENTS

Extraction solution (used hot):	Prepare a cold saturated solution of sodium acetate, filter, add two volumes of water, and add 25 ml glacial acetic acid per litre.
Acetate wash solution (used hot):	Dilute 50 ml cold saturated sodium acetate solution to 1000 ml with water.
Hydrochloric acid mixture:	To 1000 ml of clear saturated sodium chloride solution add 300 ml dilute (1:1) hydrochloric acid.
Sulphuric acid wash, 1%:	10 ml sulphuric acid in 990 ml water.

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Potassium dichromate solution saturated:

Standard sodium thiosulphate solution, 0.1N:

Starch solution: 1 gm soluble starch in 100 ml boiling water. Boil 1 minute. Cool, add 3 gm KI.

PROCEDURE

A. Decomposition of Sample

Weigh 0.5 to 5 gm of sample, containing up to 0.1 gm lead, into a 250-ml beaker. Add 20 ml hydrochloric acid, let stand at room temperature for 15 minutes or more, and then warm for 20 to 30 minutes. If sulphides remain undecomposed, cool, add 5 ml nitric acid, and continue heating. Finally, add 5 to 10 ml more hydrochloric acid and heat to dissolve all the lead chloride.

Add 10 to 20 ml 1:1 sulphuric acid (depending on the amount of sample) and evaporate to fumes. Fume twice on the hot plate to expel the volatile acids. Cool. Add about 30 ml water, rinsing down the sides and cover glass, and heat to boiling. Digest until all ferric sulphate is in solution. Then cool, add 10 ml ethyl or methyl alcohol, and cool below room temperature. Filter through a 9-cm paper (Whatman No. 42). Wash with cold 1% sulphuric acid solution, and give the beaker one final rinse with cold water. (Retain the beaker unless barium is absent.)

B. Solution of Lead Sulphate

1. *In the Absence of Barium*

Open the paper carefully and wash as much of the residue as possible into a 250-ml Erlenmeyer flask through a funnel, using hot water, and a minimum of it. Digest the paper in 25 ml hot extraction solution in a small beaker, and filter into the above flask. Wash the beaker, paper, and funnel, with hot extraction solution. Heat the flask until all the lead sulphate has dissolved. Adjust to a volume of about 150 ml.

2. *If Barium May Be Present*

Wash the residue back into the beaker, using hot water and a minimum of it. Wash under the fold of the paper to get all the loose residue possible. Leave the paper on the funnel. To the contents of the beaker add 10 ml hydrochloric acid, and evaporate almost to dryness on the steam bath. Add 25 ml extraction solution, heat to boiling, and digest. Continue adding extraction solution as necessary, up to a maximum of 75 ml total, until all the lead sulphate is dissolved. Filter through the original filter paper into a 250-ml Erlenmeyer flask, and wash the residue with hot water. Discard the paper and residue. Adjust the volume of solution to about 150 ml.

C. Precipitation of Lead Chromate

Heat the solution to boiling and add, by pipette, 10 ml of a saturated solution of potassium dichromate. Boil gently for 5 to 10 minutes. Add a solution of 2 gm citric acid in a little hot water (unless bismuth is known to be absent).

Filter at once, and wash the flask, paper and precipitate, ten times with 10-ml portions of hot "acetate wash solution". Discard the filtrate, but reserve the filter and flask.

D. Solution and Titration of Chromate

Place the washed flask under the funnel, dissolve the precipitate with hydrochloric acid mixture, and wash the precipitate and paper with the same mixture, using at least 50 ml in all. Continue the washing with 50 ml cool water.

To the solution add a solution of 1 to 2 gm potassium iodide in a little water, and stir gently. Titrate at once with a standard solution of sodium thiosulphate until the colour of iodine is almost gone, add 5 ml starch solution, and continue the titration until the colour of the solution changes to a clear green with no tinge of blue. Record the titration.

CALCULATIONS

$$\% \text{ Pb} = \frac{\text{Titration (ml)} \times 0.00691 \times 100}{\text{sample weight}}$$

If the titration for the sample is less than 0.5 ml, the lead content should be reported as "less than" the minimum amount detectable. This value is dependent on the sample weight and should be calculated as above, i.e.

$$\% \text{ Pb} = \frac{\text{less than } 0.5 \times 0.00691}{\text{sample weight}} \times 100$$

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The Determination of Radium in Natural Waters

METHOD Ra-1

SCOPE

The method described here is intended to provide a rapid estimate of the Ra^{226} content of natural waters. It is not primarily intended for use on barren solutions from uranium mills and refineries, or other concentrated sources of α-active natural isotopes.

RANGE

The lower limit for the method, using the equipment and procedure described, is about $3\mu\mu$ c of Ra^{226} in the sample taken for analysis. With the usual 12-ounce sample this is roughly $10\mu\mu$ c of Ra^{226} per litre. By using α-counting equipment with a lower background and longer counting times this lower limit could be reduced proportionately.

APPARATUS

Millipore filter apparatus:	(available from Millipore Corp , Watertown, Mass , U.S.A.) consisting of solution-container, sintered glass base, and clamp (*see* Figure 1).
Flasks, filtering, heavy wall with tubulature:	1000 ml size.
Millipore filters HA:	47 mm dia., black hydrosol assay type.
Source of vacuum for filtering:	
Beakers, Griffin low-form:	600 ml size, 150 ml size.
Pipette:	25 ml size.
Rubber bulbs for pipetting:	
Flask, volumetric:	2000 ml size, 250 ml size.
Graduated cylinders:	500 ml size.
pH meter:	
Hot plate:	An oscillating hot plate is convenient.
Alpha counting equipment:	*See* Figure 2 for details of scintillation counter and scaling equipment used.
Dishes, counting:	Aluminum dishes, 50 mm dia., 6 mm deep (to hold Millipore filters).

REAGENTS

NOTE: Use deionized water throughout as both tap and distilled water give consistently high blanks.

Standard radium stock: either solution

(a) U.S. National Bureau of Standards Ra^{226} gamma-ray standard containing 1.0×10^{-7} gm Ra. Break the ampoule under a litre of deionized water. Leach the broken ampoule with 50 ml concentrated hydrocholoric acid and wash with deionized water. Add the leach and the washings to the original solution. Dilute to 2 litres. 1 ml = 5×10^{-11} gm/l of radium.

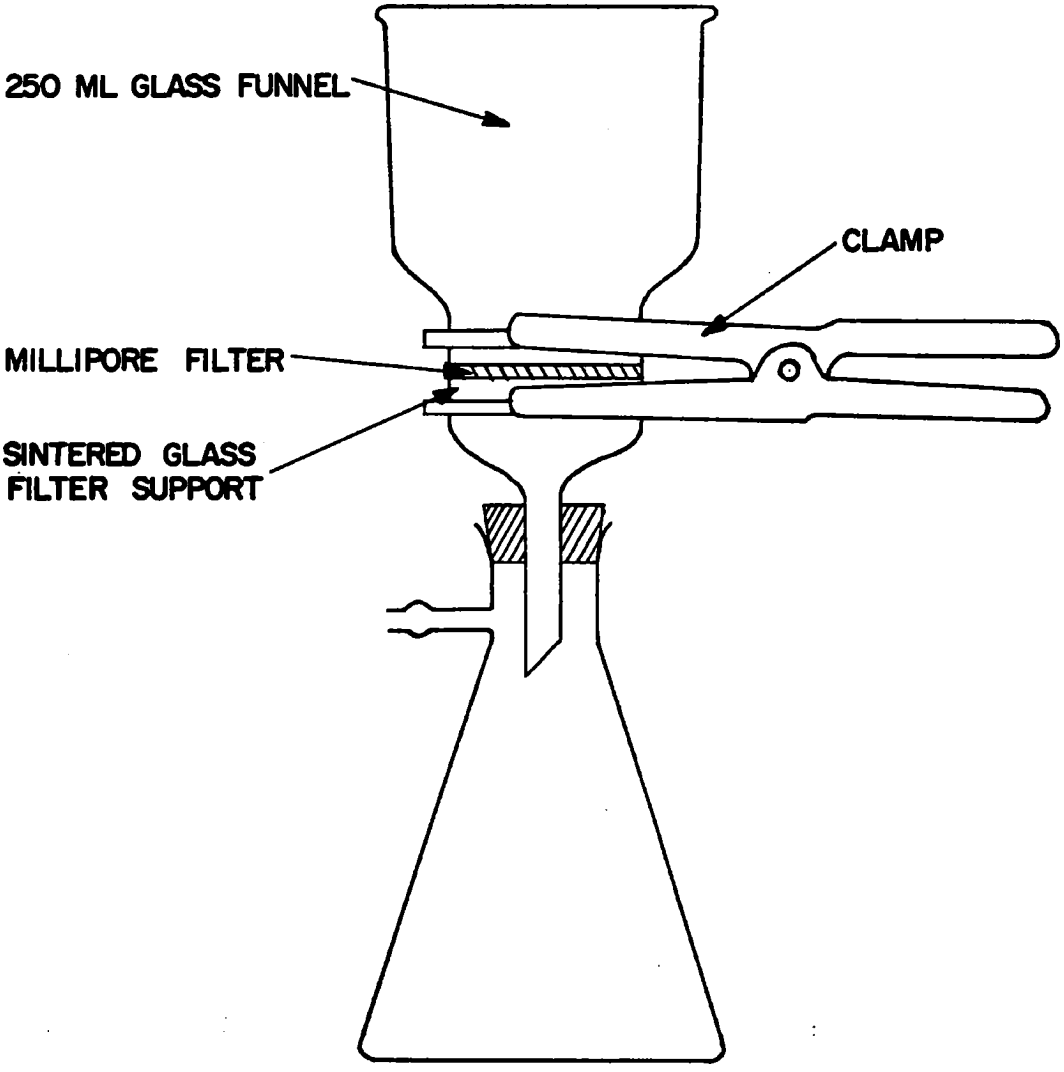

FIGURE 1

MILLIPORE FILTER APPARATUS

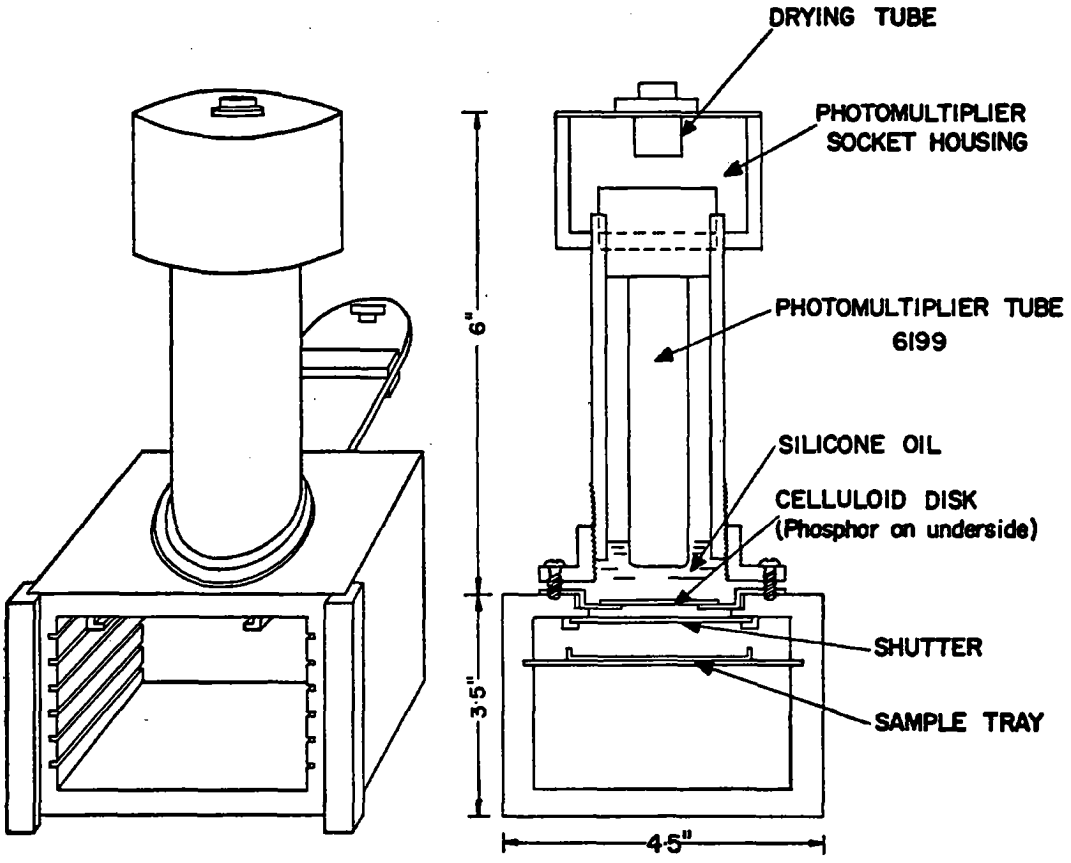

FIGURE 2

ALPHA SCINTILLATION DETECTOR

Standard radium stock— *continued:*

(b) Weigh out accurately into a 150 ml beaker, a sufficient quantity of a uranium ore in equilibrium to provide 0.3 gm U_3O_8 ($\doteq 1 \times 10^{-7}$ gm Ra) (Port Radium pitchblende, 53% U_3O_8 has been used here). Moisten and add 25 ml of 1:1 nitric acid. Cover the beaker and boil for at least 1 hour. Dilute to 50 ml and filter through a Whatman No. 42 paper into a 250 ml beaker. Wash the beaker and paper thoroughly with warm water.

Ignite the filter paper and residue in a platinum crucible. Moisten the ash, add 5 ml hydrofluoric acid and take to dryness. Moisten with perchloric acid and fume several times to expel fluoride. Add about 2 gm sodium carbonate and fuse for 1 hour over a flame. Cool and dissolve the melt in nitric acid. Add this solution to the solution in the 250 ml beaker. Take the combined filtrates to dryness. Moisten with hydrochloric acid and take to dryness several times

Standard radium stock—*concluded:* with more hydrochloric acid to expel nitrate. Finally add 5 ml hydrochloric acid and 50 ml of water. Warm to dissolve and transfer to a 2 litre volumetric flask. Add 50 ml concentrated hydrochloric acid and dilute to 2 litres.

1 ml = 0.15 mg U_3O_8 = 5×10^{-11} gm Ra.

Standard radium working solution: Transfer* 25 ml of either stock solution, (a) or (b), to a 250 ml volumetric flask, add 5 ml concentrated hydrochloric acid and dilute to 250 ml with deionized water.

* WARNING: Use rubber bulbs for pipetting. DO NOT PIPETTE BY MOUTH.

Hydrochloric acid solution (for pH adjustment): 0.5N, in deionized water.

Sodium hydroxide solution (for pH adjustment): 0.5N, in deionized water.

Barium carrier solution: 2.5 gm $BaCl_2 \cdot 2H_2O$ in 1 litre deionized water.

Ammonium sulphate solution: 400 gm $(NH_4)_2SO_4$ in 1 litre of hot deionized water. Cool and filter.

Sulphuric acid wash solution: 5 ml of concentrated sulphuric acid in 1 litre of deionized water. Add 1-2 drops of Aquet (a non-ionic wetting agent).

PROCEDURE

NOTE: Do not start more samples than can be counted the next day.

Measure the volume of the sample in a graduated cylinder, and transfer as completely as possible to a beaker of suitable size. (The usual sample size is 350 ml and a 600-ml beaker is used). At the same time take two equivalent portions of deionized water. To one add 1 ml, to the other 5 ml of the working radium standard. (Warning: Use a rubber bulb for pipetting). Carry out a reagent blank as well.

Using a pH meter, adjust the pH of all the solutions to 3.0 $\pm$ 0.25 using 0.5N hydrochloric acid or 0.5N sodium hydroxide, as required. Transfer the beakers to an oscillating hot plate. Heat them almost to boiling and add 3 ml of barium chloride solution to each. Stir vigorously and add 15 ml of ammonium sulphate solution. Allow the hot plate to oscillate for 15 minutes. (If an oscillating hot plate is not available, stir frequently for 15 minutes). Remove from the hot plate and let stand for 4 hours.

Assemble the Millipore filter apparatus, with a 47-mm H A, black (plastic) Millipore filter in place over the sintered glass, and insert in the 1000-ml filtering flask. Decant the clear liquor through the filter, and finally transfer the bulk of the precipitate to the filter. Wash with three 25-ml portions of sulphuric acid wash solution, making sure to wash down any precipitate on the walls of the filter apparatus.

Disassemble the filter apparatus and transfer the plastic filter sheet to a numbered aluminum dish, with one of the paper nutrient pads (supplied with the filters) underneath it. Dry 30 minutes at 110° C. Cool and store in a clean place.

The next day, transfer the filter discs, still in the aluminum dish, to the chamber of the alpha-counting apparatus. Count for a sufficient length of time to give the required precision as determined from Figure 3, and record the count. Make a background count, using an empty aluminum dish, before counting the samples, and after the counting has been completed. This should give substantially the same count as the reagent blank. Subtract the count of the blank from the count of the samples and standards run at the same time. Record

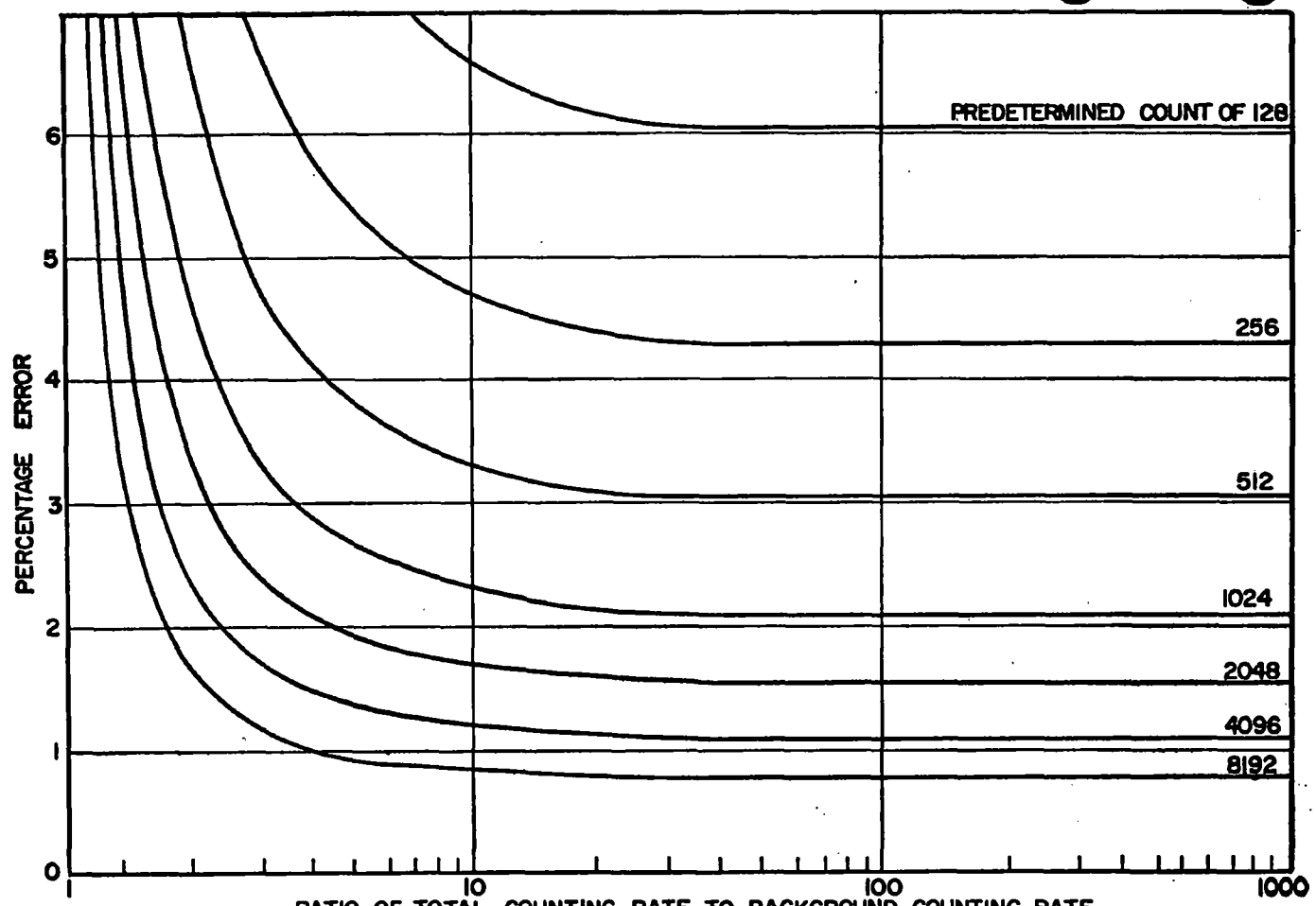

FIGURE 3

STATISTICAL ERROR AS A FUNCTION OF THE TOTAL COUNT-RATE/BACKGROUND COUNT-RATE RATIO FOR VARIOUS TOTAL COUNT LEVELS

this as the net count. Plot a graph of net counts of the standards against the contained radium content in micro-microcuries. Read the radium content of the samples from this graph and calculate the radium content of the samples in micro-microcuries per litre.

CALCULATIONS

$$\mu\mu \text{ c Ra/l} = \frac{\mu\mu \text{ c in ppt. (from graph)}}{\text{vol. of sample}} \times 1000$$

The limit of detection with the equipment used here is about $3\mu\mu$ c of Ra^{226} in the sample taken for analysis. If the count rate observed is close to background the result should be reported as "less than" the concentration that corresponds to this value.

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The Gravimetric Determination of Combined Rare Earth Oxides and of Combined Rare Earth Oxides plus Thorium Oxide, in Ores, Mill Products and Solutions

METHOD R.E.-1

SCOPE

The method is intended for the determination of combined rare earth oxides, or combined rare earth oxides and thorium, in ores and solutions for mill control, and in the uranium concentrates for control and for specification purposes.

RANGE

The lower limit for ores is 0.5%, for solutions about 0.5 gm/l and for uranium concentrates about 0.05%, since in general no precipitate forms unless about 3 mg rare earths are present. It is possible to take a larger sample of the concentrate, hence the limit is lower.

OUTLINE

The rare earth separation is based primarily on the methods described by Carron *et al.* (1). In the case of uranium concentrates and iron-gypsum precipitates, it is necessary to take a larger sample to achieve the required sensitivity and this is made possible by using an ion exchange procedure (anion exchange from 10N HCl) (2, 3) to remove the bulk of the uranium and iron. The ion exchange procedure is also supposed to remove zirconium, niobium, tantalum, molybdenum and tungsten (4), but this point has not been investigated here.

The use of a carbonate treatment for solubilizing alkaline earth sulphates and for eliminating sulphate (by metathesis) from samples which consist primarily of these salts, will result in the loss of some of the rare earths due to the formation of soluble rare earth complex carbonates. Thus it has been found that Y, Sm and Gd are almost completely soluble, while La, Ce, Pr and Nd are only slightly soluble in carbonate solution (6, 7). Table 1 of reference 7 shows the extent of this solubility. If the carbonate solution is discarded the former elements are lost. The supernatant carbonate-sulphate solution is therefore separated from the metathesized carbonate precipitate, acidified, boiled to remove CO_2, and the rare earth elements precipitated with ammonia using iron as a carrier.

Thorium and rare earth oxalates are then precipitated at least twice at pH 2, using calcium both as a carrier and also to indicate whether precipitation has been complete. This effects the removal of all elements except the rare earths, thorium, actinium, scandium, yttrium, calcium, strontium and gold. Some barium, manganese, cobalt, nickel, copper, zinc, silver, cadmium, tin, lead and

bismuth, if present, will also precipitate. Most of the magnesium (a major constituent of magnesium diuranate precipitates), will be removed. Ammonium hydroxide precipitation above pH 10 removes the bulk of these elements from the rare earths and thorium, except possibly scandium, yttrium, tin, lead and bismuth, if present.

The rare earths may then be freed from thorium by precipitation of the thorium using sebacic acid at pH 2.5. The rare earths sebacates are precipitated in the filtrate by raising the pH to 9. They are ignited to the oxides, weighed, and submitted to the spectrographic laboratory for determination of individual rare earths, thorium and other major constituents. The result obtained is corrected for constituents other than rare earths, and reported as $(RE)_2O_3$. For the purposes of the method, the rare earths are assumed to be lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium and ytterbium. Yttrium is *not* included. It is often found in the precipitates, but recovery is not quantitative, and in any case it is not, strictly speaking, a rare earth.

In general, it has been found that with samples containing more than 1% rare earths, the precipitates are quite free of contaminants. With ores containing small amounts of rare earths, aluminum is a frequent contaminant, especially if the fluoride-aluminum nitrate attack is used. It can be eliminated by carrying out several additional oxalate separations, as recommended under "Procedure", Section B.

Lead tends to carry through the procedure, and being a common constituent of radioactive ores, is often found in the precipitates. It can easily be eliminated by many well-known procedures (H_2S precipitation, electrolysis, dithizone extraction) if desired, but these do not form part of the present method.

For routine work on samples low in thorium, especially ores, the thorium-rare earth separation and spectrographic check can be omitted. The result can be corrected for the thorium content which will have been determined on a separate sample by the mesityl oxide colorimetric method (5), in most cases, or on the rare earth precipitate, by the simple colorimetric procedure given in this method.

APPARATUS

Centrifuge:	Similar to International Size 1 Model C50, with 4-place, 250-ml head.
Centrifuge bottles:	250-ml capacity, Pyrex glass similar to Fisher 5-586.
Centrifuge bottles, polyethylene:	8-oz. capacity, wide mouth, made from low-pressure (Ziegler) or other heat-resistant polyethylene e.g., New Brunswick Scientific Supply Cat. No. 1204 WMHH 8 oz. or 1210-2 HH 250 ml.
Centrifuge:	Similar to International Clinical model with 4-place, 50-ml head.
Harvard trip scale:	2000 gram cap., 0.1 gram sensitivity, for balancing centrifuge bottles
Burettes, dispensing:	Straight stopcock, Pyrex glass 250 ml capacity (for use as ion exchange columns).
Funnels:	Bunsen filtering, long stem, Pyrex glass, fluted, 65 and 75 mm dia.
Support, funnel:	6-hole model.
Platinum dishes:	50-ml cap. and 150-ml cap.
pH meter:	
Glass and calomel electrodes:	

pH short range test papers:	Range 1.0 to 2.5 Range 3.0 to 5.5 Range 8.0 to 9.5 Range 10.0 to 12.0.
Graduated cylinders, pharmaceutical:	30, 60 and 120 ml.
Filter paper:	Whatman No. 40, 41H, 42 in 12.5 cm, 11 cm, 9 cm and 7 cm sizes.
Porcelain crucibles, high form:	Coors size 1.
Steam bath:	
Muffle furnace:	Capable of giving a temperature of 1000° C for ½ hour.

REAGENTS

Sodium peroxide, C.P.:	
Sodium carbonate wash solution, 1%:	10 gm Na_2CO_3 per litre distilled water.
Nitric acid, concentrated:	
Nitric acid, dil.: 10% v/v:	Dilute 100 ml concentrated acid to 1 litre with water.
Hydrofluoric acid, concentrated (48%):	Reagent grade.
Hydrofluoric acid, dil. (10%):	Dilute 100 ml of the 48% acid to 500 ml with water. Handle in plastic equipment only.
Hydrofluoric acid, dil. (1%):	Dilute 10 ml of the 48% acid to 500 ml with water.
Potassium fluoride, *anhydrous:*	Granular, reagent-grade material.
Sodium bisulphate, C.P.:	
Aluminum nitrate solution:	190 gm $Al_2(NO_3)_3 \cdot 9H_2O$ in 85 ml water and 15 ml concentrated nitric acid. Warm to dissolve and store in a covered container in a warm place.
Sodium carbonate; anhydrous, fine granular reagent:	
Perchloric acid, 70%:	
Anion exchange resin:	Amberlite IRA400 or XE 117 (a finer mesh fraction of the same resin) (Rohm and Haas Co., Philadelphia).
Hydrochloric acid, 10N:	Take 1670 ml of concentrated HCl (CP) and dilute to 2 litres.
Methyl oxalate, alcoholic:	Heat reagent grade oxalic acid dihydrate in an oven at 100° C for 3 hours (not longer). Break up the crust and heat another hour. When cool, dissolve 40 grams of anhydrous oxalic acid in 100 ml of reagent grade methanol. Let stand at least 3 days. Filter before using. 15 ml of this solution provides 4 grams of oxalate ion. In an emergency a solution of 53 grams of methyl oxalate in 100 ml of methyl alcohol can be used without waiting.
Calcium nitrate solution:	Dissolve 2 grams of CP calcium nitrate in 500 ml of distilled water. Adjust to the green colour of bromophenol blue indicator with very dilute nitric acid; 5 ml are equivalent to 0.05 gm CaO.

Sodium hydroxide solution, 50%:	Dissolve 200 grams of reagent grade NaOH in 250 ml of water. Let stand overnight, decant and dilute to 400 ml. A 50% solution can also be purchased. Store in polyethylene.
Ammonium hydroxide S.G. 0.90:	Must be fresh.
Bromophenol blue indicator:	Dissolve 0.1 gram of water soluble bromophenol blue in 100 ml of water.
Thymol blue indicator:	Dissolve 0.04 gram of thymol blue in 100 ml of 60% ethyl alcohol.
Ammonia-ammonium nitrate wash solution:	Dissolve 5 grams of reagent grade ammonium nitrate in 475 ml of distilled water and add 25 ml of ammonium hydroxide, specific gravity 0.90.
Oxalic acid wash solution:	Dissolve 5 grams of reagent grade oxalic acid dihydrate in 500 ml of distilled water.
Hydroxylamine hydrochloride:	Reagent grade.
Sebacic acid solution:	50 grams of CP sebacic acid per litre of methanol.
Ammonium sebacate solution:	Dissolve 0.75 gram sebacic acid, C.P., in 18 ml of distilled water and 1.5 ml of ammonium hydroxide, S. G. 0.90.

PROCEDURE

A. Preliminary Treatment

1. *Ores*

Weigh 0.5 to 2.0 gm of sample into a 150-ml platinum dish. Add 1 ml of calcium nitrate solution (10% w/v), followed by 10-20 ml of concentrated hydrofluoric acid, and evaporate almost to dryness. Repeat the hydrofluoric acid treatment three times. Add about 50 gm anhydrous potassium fluoride, mix, and fuse over a Fisher blast-burner using propane gas for 2 minutes or until the melt becomes clear (do not fuse for an excessively long time). Cool, add 100 ml of hydrofluoric acid, and heat gently in a well-ventilated hood for 30 minutes to break up the fusion and dissolve the undesired constituents (thorium, rare earth, lead, aluminum, calcium and magnesium fluorides are insoluble). Transfer to a 250-ml wide-mouth polyethylene centrifuge bottle, using more hydrofluoric acid if necessary to complete the transfer. Carefully counterbalance the bottles and centrifuge them for 5 minutes. Decant and discard the clear supernatant solution. Add about 100 ml of dilute (12%) hydrofluoric acid solution and stir well using a plastic stirring rod. Centrifuge for 5 minutes, and again decant and discard the clear supernatant liquid. To the precipitate in the bottle, add 10 ml of aluminum nitrate solution and 5-10 ml of concentrated nitric acid. Warm to dissolve, and transfer to a 250-ml glass beaker.

Proceed to Section B, "Precipitation with Alcoholic Methyl Oxalate Solution".

2. *Ores (alternative procedure)*

Ignite 0.5 to 2.0 grams of sample in a porcelain crucible at dull red heat (500° C) to expel moisture. Add 6 to 8 grams of sodium peroxide and fuse at dull red heat for 1 minute. Cool. Transfer the crucible to a 400-ml beaker and leach the fusion product in 200 ml of water. Digest the solution on the steam bath for 30 minutes and let stand overnight at room temperature. Filter the solution through a double filter paper, one 12.5-cm Whatman No. 42 above one 12.5-cm Whatman No. 41H filter paper, previously rinsed with 1% sodium carbonate wash solution. Wash eight to ten times with 1% sodium carbonate

solution. Discard the filtrate (silicon, aluminum, phosphorus and sodium salts). Wash the precipitate from the papers with a stream of water into the original beaker. Pass through the papers in small portions at a time, 50 ml of hot 10% nitric acid containing 5 ml of 30% hydrogen peroxide. Rinse the papers with water. Heat the beaker until dissolution of the precipitate is complete. Remove from the hot plate, and thoroughly police and rinse the crucible. Ignite the papers in the crucible and add the ash to the solution.

Evaporate the solution to dryness. Take up with 5% nitric acid containing 1 gram of hydroxylamine hydrochloride. Separate the residue, (retaining the main aqueous solution), transfer it to a platinum dish, and volatilize the silica with a few ml of hydrofluoric acid. Fuse any residue remaining with 1 gram of sodium bisulphate. Dissolve the melt in 50 ml of water. Bring the solution to boiling and add 50% sodium hydroxide sufficient to provide 5% excess. Digest on the steam bath for 20 minutes. If no precipitate appears, discard the solution. If a precipitate forms, filter the solution through a small No. 40 paper, and wash the precipitate ten times with hot 1% sodium carbonate solution, and discard the filtrate and washings. Transfer the precipitate and paper to the main solution and adjust the volume to 125 ml.

Proceed to Section B.

3. *Solutions*

Pipette 50 ml of solution into a 250-ml beaker. Add 100 ml water, boil and add 50% sodium hydroxide in excess. Digest 20 minutes on the steam bath. Transfer to a 250-ml centrifuge bottle and centrifuge 15 minutes at 1500 r.p.m. Discard the supernatant and wash the precipitate three times by repulping with hot 1% sodium carbonate solution and centrifuging. Transfer the bulk of the precipitate to a 250-ml beaker, completing the transfer with 50 ml of hot 10% nitric acid containing 5 ml of 30% hydrogen peroxide. Rinse the centrifuge bottle into the beaker with water and make the solution in the beaker to 125 ml.

Proceed to Section B.

4. *Gypsum Cake*

Weigh out a 80-gm sample into a 400-ml beaker. Add 50 gm of sodium carbonate, mix well and add 20 ml water while stirring. Digest 1 hour on the steam bath. Transfer to a 250-ml centrifuge bottle. Centrifuge 15 minutes at 1500 r.p.m. Decant the supernatant solution into an 800-ml beaker. Wash the precipitate twice with 150 ml of hot 1% sodium carbonate solution, centrifuging each time. Add the washings to the beaker.

Carefully acidify the carbonate wash solution with concentrated hydrochloric acid and boil 10 minutes to expel CO_2. Add a few drops of saturated ferric chloride solution followed by a few drops of methyl red indicator (0.2% alcoholic solution). Stir well, and add dilute ammonium hydroxide (1 : 1) dropwise until the solution is distinctly coloured yellow. Boil the solution for at least 10 minutes, and filter hot on a small Whatman No. 41H paper. Do not wash. Discard the filtrate and place a clean 400-ml beaker under the funnel. Dissolve the precipitate on the paper with a minimum of concentrated hydrochloric acid and wash it completely into the beaker with hot water. Dissolve the precipitate in the centrifuge bottle in a minimum of hydrochloric acid, also, and transfer this solution to the same 400-ml beaker. Dilute to 200 ml

and boil 10 minutes. Add a few drops of methyl red indicator, and add dilute ammonium hydroxide dropwise till the solution is distinctly yellow. Digest 20 minutes on a steam bath.

Centrifuge and wash as before, using hot 1% ammonia for washing, in place of sodium carbonate and discard the washings. Dissolve the precipitate in a minimum of concentrated hydrochloric acid, transfer to a 400-ml beaker and take to low volume on a hot plate or steam bath. Make to 80 ml using 10N hydrochloric acid and carry out the ion exchange procedure and subsequent treatment as for "Uranium Concentrates".

5. *Uranium Concentrates* (*Carry out duplicate determinations.*)

Weigh out a 20-gram sample of the high-grade precipitate into a 250-ml beaker. Dissolve in 30 ml concentrated hydrochloric acid, warming and stirring as required. Transfer to a 50-ml centrifuge tube and centrifuge 15 minutes to remove insoluble matter. Decant the supernatant solution into a clean 250-ml beaker. Rinse the original beaker (into the centrifuge tube) with a 25-ml portion of concentrated hydrochloric acid. Stir up the insoluble residue with the acid, centrifuge again and decant the wash into the same beaker as the initial supernatant solution. Rinse the beaker into the centrifuge tube with 20 ml of water, stir up the residue again and centrifuge as before. Decant the water wash into the beaker.

Transfer the insoluble residue to a 50-ml platinum dish with water. Add 5 ml hydrofluoric acid and take to dryness. Add 5 ml more of hydrofluoric acid and again take to dryness. Add perchloric acid and fume to dryness twice with 5-ml portions and finally fuse the residue remaining with 5 gm sodium carbonate, take up in water and filter. Discard the filtrate. Dissolve the residue in a minimum of concentrated hydrochloric acid. Dilute to 100 ml, boil and precipitate with ammonia. Filter and discard the filtrate. Dissolve the precipitate in a minimum of concentrated hydrochloric acid ($\backsim$ 5 ml) and add to the main solution.

Prepare a 200-ml column of IRA 400 or XE 117 by passing 250 ml 10N hydrochloric acid at 10 ml/min and drain down to the top of the bed. Place a clean 400-ml beaker under the column and pass the sample through the column at a rate of 5 ml/min (2 drops/sec). Do not add all the sample at once, but add approximately 20-ml portions at a time and let them drain down close to the top of bed (to prevent channelling). Discard the first 20 ml of effluent. Use the next 40 ml of effluent to rinse the beaker and return this to the top of the column. Do the same with the next 40 ml of effluent. Then add three 80-ml portions of 10N HCl, letting each drain down to the top of the bed before adding the next portion.

Put the beakers containing the effluent on the steam bath and let them evaporate overnight.

Wash the resin columns with water till no more colour is observed, then with 0.5 N HCl and finally with 10 N HCl, ready for the next sample.

Dissolve the contents of the beaker in about 200 ml of water. Heat to boiling and add 50% sodium hydroxide in excess. Digest 20 minutes on the steam bath. Transfer to a 250-ml centrifuge bottle and centrifuge 15 minutes at 1500 r.p.m. Discard the supernatant liquid and wash the precipitate three times by repulping with hot 1% sodium hydroxide solution and centrifuging. Transfer the bulk of the precipitate to a 250-ml beaker, completing the transfer with 50 ml of hot 10% nitric acid containing 5 ml of 30% hydrogen peroxide.

Rinse the centrifuge bottle into the beaker with water and make the solution in the beaker to 125 ml.

Proceed to Section B.

6. *Thorium Oxalate, Carbonate and Hydroxide Precipitates*

Weigh out a suitable portion of the sample, (containing 10 mg rare earth oxides, if possible). Transfer to a 400-ml beaker, moisten with water, and cautiously add 50 to 75 ml of concentrated nitric acid. Cover with a watch glass and digest at low heat on a padded hot plate or under infra-red lamps. If the sample does not dissolve readily, remove the watch glass and boil for about 30 minutes.

A white residue may consist of titanium dioxide. If this is suspected, add 5 ml of 30% hydrogen peroxide and boil again. A deep yellow or orange colour confirms the presence of titanium and serves to indicate whether further peroxide additions will be of value.

If the sample is still refractory, add a few drops of 1% hydrofluoric acid solution and continue boiling, repeating the addition of 1% hydrofluoric acid from time to time, but avoiding the addition of quantities sufficient to cause thorium to precipitate.

When the sample is substantially dissolved, filter off the insoluble residue, if large. Transfer the filter paper and contents to a 50-ml platinum dish, dry and ignite it at low temperature. Cool, moisten, add 5 ml concentrated hydrofluoric acid and evaporate to dryness. Repeat the hydrofluoric acid treatment and again take to dryness. Add perchloric acid, fuming to dryness twice with 5-ml portions, and finally fuse the residue remaining with 5 gm sodium carbonate. Take up in water, filter and discard the filtrate. Place a clean 250-ml beaker under the funnel, and dissolve the residue into the beaker with a minimum of 1:1 nitric acid. Dilute to about 100 ml, boil and precipitate with ammonia. Filter and discard the filtrate. Place the same beaker under the funnel and dissolve the precipitate into it with a minimum of hot 1:1 nitric acid. Add this solution to the main body of sample solution.

Evaporate the solution down to about 25 ml.

If hydrofluoric acid was used in dissolving the sample, cool, add 20 ml of perchloric acid and take to fumes. Cover the beaker with a watch glass and let reflux for 15 minutes.

In either case, cool, and dilute to 125 ml with water.

Proceed with Section B.

B. Precipitation with Alcoholic Methyl Oxalate Solution

To the solution add 10 ml of calcium nitrate solution (equivalent to 0.1 gram of calcium oxide), unless the sample is known to contain calcium as a major constituent. Add 5 to 10 ml of 30% hydrogen peroxide. Heat the solution on a steam bath, add 4 drops of bromophenol blue indicator solution, then add 50% sodium hydroxide dropwise and with vigorous stirring to pH 3.8 as indicated by the blue-green colour of the indicator (or use pH paper). Add 15 ml of prepared alcoholic methyl oxalate solution slowly and with stirring. With the beaker uncovered, digest the solution 30 minutes on the steam bath, maintaining the volume at 125 ml by adding distilled water if necessary. Remove

the beaker from the steam bath and adjust the pH to 2.0 with 50% sodium hydroxide solution using suitable indicator paper. Let the solution stand 1 hour.

Pour the supernatant liquid into another beaker, or if the liquid is not clear, filter about 75 ml of it through a 9-cm Whatman No. 42 paper. Reserve the paper for subsequent filtering. Add 5 ml of calcium nitrate solution. Stir and let stand until a precipitate forms. Precipitation of calcium oxalate within 2 minutes indicates that thorium and rare earth precipitation is complete. Return the solution and precipitate to the beaker to stand another hour. If the added calcium had precipitated in the supernatant liquid within 2 minutes, add 5 ml more of calcium nitrate solution directly to the beaker and stir. (Otherwise repeat the transfer of the supernatant liquid or the filtration and the treatment with 5 ml of calcium nitrate solution until precipitation occurs within 2 minutes.) Let the solution stand 30 minutes and filter it through a 9-cm Whatman No. 42 paper (or the reserved paper). Wash the precipitate eight to ten times with 1% oxalic acid. Transfer the paper and precipitate to the original beaker, add 20 ml nitric acid, cover, and destroy paper and oxalate by gently boiling until a few ml remain. Evaporate to dryness on the steam bath. Dissolve the salts in 50 ml of 5% nitric acid containing 5 ml of 30% hydrogen peroxide by digesting on the steam bath till clear. Adjust the volume to 125 ml, heat on the steam bath, and repeat the entire procedure for precipitating the rare earth and thorium oxalates, omitting further addition of calcium nitrate solution except for tests on the supernatant liquid. In the case of ore samples or other samples containing large amounts of aluminum, repeat this precipitation at least twice more.

Finally, destroy the paper and oxalates in the original beaker by boiling with 20 ml of concentrated nitric acid until only a few ml remain. Evaporate to dryness on the steam bath and let bake for 30 minutes.

C. Separation of Calcium from Thorium and Rare Earth Elements

To the dry nitrates add 1 ml of 1 : 1 nitric acid, 25 ml of water and 0.5 gram of hydroxylamine hydrochloride. Digest on the steam bath until completely dissolved. Cool the solution to room temperature and dilute to 100 to 125 ml. Add concentrated ammonium hydroxide with constant stirring to pH over 10 (using pH paper). Add 5 ml of ammonium hydroxide in excess and some paper pulp and let the precipitate stand 1 hour at room temperature; stir occasionally. Filter the solution through a Whatman No. 40 filter paper, previously rinsed with ammonia-ammonium nitrate wash solution and wash six times with the same solution. Drain the excess ammonia from the precipitate by applying gentle suction.

This precipitate can be handled very conveniently by centrifuging. If much calcium and magnesium are present, redissolve the precipitate in a minimum of nitric acid and reprecipitate as described. Use the calibrated 50-ml centrifuge tubes and redissolve and reprecipitate until there is no significant diminution in precipitate volume.

If the combined rare earth oxide and thorium oxide content is being determined, proceed to Section F, omitting Sections D and E.

If the combined rare earth oxide determination is required, continue with the following section.

D. Separation of Thorium From Rare Earth Elements

Transfer the precipitate and paper to the original beaker, add 20 ml of concentrated nitric acid and destroy the paper by gentle boiling. Evaporate to dryness. Dissolve the salts in 25 ml of water containing 1 ml concentrated nitric acid. Dilute to 75 ml, add 2 grams of hydroxylamine hydrochloride and 1 ml of

thymol blue indicator. Adjust the pH to 2.6 using nitric acid or ammonia. Heat the solution to boiling. Slowly and with constant stirring add 10 ml of methanolic sebacic acid solution containing 2 drops of 5% nitric acid. (This amount is sufficient for 0.1 gram ThO_2—in analyzing a concentrate containing 2% ThO_2, use 40 ml of the sebacic acid solution.) Add a small amount of paper pulp and digest the precipitate on the steam bath for 10 minutes. Quickly filter the solution through a Whatman No. 42 paper and wash the precipitate fifteen times with nearly boiling water acidulated with nitric acid to the bright orange of thymol blue*. Discard the filtrate.

If the sample is high in thorium, transfer the precipitate to the original beaker, dissolve it in nitric acid and repeat the thorium separation, once more if the rare earth content is high, twice if it is low.

Finally, ignite and weigh the thorium precipitate and submit for spectrographic determination of rare earths, correcting the weight of the final rare earth precipitate for any rare earths in the thorium precipitate.

E. Precipitation of Rare Earth Elements

Adjust the volume of the filtrate to 150 ml and cool to room temperature (excess sebacic acid crystallizes on cooling). Add concentrated ammonium hydroxide dropwise to pH 9, using pH paper. Add 20 ml of ammonium sebacate solution and a small amount of paper pulp. Let the precipitate stand 30 minutes with occasional stirring. Filter the solution through a Whatman No. 40 paper previously rinsed with ammonia-ammonium nitrate solution, and wash the precipitate eight to ten times with the same wash solution. Drain excess ammonia by applying gentle suction. Ignite under oxidizing conditions at 1000°C to constant weight.

Submit the precipitate to the spectrographic laboratory for rare earths and major constituents determination. Correct the weight obtained for any rare earths in the thorium precipitate and for major impurity constituents in the rare earth precipitate. Report as $(RE)_2O_3$.

If no spectrograph is available, verify the absence of thorium in the rare earth precipitate by the colorimetric procedure, Section G.

F. Precipitation of Rare Earth Elements Plus Thorium

In many cases, as for example where the thorium content is believed to be very low, the combined rare earth oxides plus thorium oxide may be determined. In such cases it is usually simpler to carry out the combined determination, then determine rare earths by difference after carrying out the colorimetric thorium determination (Section G).

Transfer the precipitate and paper from the separation of calcium (Section B), to the original beaker, and pulp the paper with 6 ml of 1:1 (v/v) nitric acid. Heat on the steam bath and dilute to 150 ml. Add a gram of hydroxylamine hydrochloride and cool to room temperature. Add concentrated ammonium hydroxide dropwise to pH 9, as indicated by pH paper. Add 20 ml of ammonium sebacate solution. Let the solution stand 30 minutes with occasional stirring.

* Speed is essential as sebacic acid tends to crystallize ont and is difficult to redissolve. Use of the centrifuge is very convenient here too, especially if the metal shield tubes are preheated on the steam bath to conserve heat.

Filter the solution through a Whatman No. 40 paper previously rinsed with ammonia-ammonium nitrate solution and wash the precipitate eight to ten times with the same wash solution. Drain the excess ammonia under gentle suction. Ignite under oxidizing conditions at 1000° C to constant weight. Report as $(RE)_2O_3 + ThO_2$.

G. Determination of Thorium Content of Combined Rare Earth-Thorium Precipitate

Apparatus

Volumetric flasks:	25 ml, 100 ml sizes.
Spectrophotometer:	Beckman Model B.
Cells, spectrophotometer:	1 cm and 5 cm path lengths.

Reagents

Hydrofluoric acid:	Reagent HF 48% diluted 1:40 v/v with water.
Thorin reagent:	0.1% Thorin in water. This solution is normally stable for several months.
Thorium solution (10 mg ThO_2 per ml):	Dissolve 10.5 grams thorium nitrate ($Th(NO_3)_4 + H_2O$) in water slightly acidified with hydrochloric acid. Make the solution up to 500 ml in a volumetric flask. Check the thorium content by an oxalate precipitation.

Preparation of Calibration Graph

Take aliquots of the thorium solution containing from 5 to 225 micrograms of ThO_2. Add 1 ml of perchloric acid. Take to dryness. Redissolve in 0.5 ml concentrated hydrochloric acid and make up to about 20 ml in a 25-ml volumetric flask. Add 3.0 ml of 0.1% Thorin reagent, and make up to volume. Read the optical density of the solution at 545 millimicrons on the Beckman Model B spectrophotometer against a blank solution prepared in exactly the same way except that no thorium is added.

Plot a graph with optical density as abscissa and micrograms ThO_2 per 25 ml volume as ordinate, using 1-cm Corex cells. A similar curve should also be prepared using the larger 5-cm cells, for use when increased accuracy is desired in the lower range.

Procedure

Weigh the whole precipitate. Transfer to a 100-ml beaker, add 5 ml concentrated HNO_3, 10 drops 1:40 HF and 15 drops concentrated $HClO_4$. Slowly bring to fumes and finally take to dryness.

Add 2 ml concentrated HCl and heat till the residue is completely dissolved. Dilute to 10 ml and transfer to a 25-ml volumetric flask. Make the solution up to volume and mix thoroughly. Pipette an aliquot estimated to contain 50 to 250 micrograms ThO_2. Transfer to a 25-ml volumetric flask.

Add 0.5 ml concentrated HCl, dilute to approximately 20 ml, add 3.0 ml of a 0.1% solution of Thorin reagent and make to volume. Measure the optical density at 545 millimicrons on the Beckman "B" spectrophotometer. Determine micrograms ThO_2 per 25 ml volume by means of the previously prepared calibration graph. As an added precaution carry three standards covering the range 0 to 250 micrograms ThO_2 through the whole procedure along with the samples.

Calculations

$$\% \ ThO_2 = \frac{\gamma \ ThO_2 \text{ per 25 ml (from graph)}}{1{,}000{,}000} \times \frac{\text{final sol. vol.}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

CALCULATIONS

$$\% \ (RE)_2O_3 = \frac{\text{wt. ppt.}}{\text{wt. sample}} \text{ (corrected for major impurities)} \times 100$$

If no precipitate is obtained, the rare earth content should be reported as "less than" the minimum amount detectable based on the sample weight taken. The minimum amount detectable is about 3 milligrams for this method so that the value to report would be

$$< \frac{0.003}{\text{wt. sample}} \times 100$$

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The Gravimetric Determination of Sulphur as Barium Sulphate

METHOD S-1

SCOPE

This method covers the determination of sulphate, and of those forms of sulphur which can conveniently be converted to sulphate, using the preliminary treatment to differentiate between the states in which the sulphur was originally present.

Procedures for the following separate determinations are described.

A. *Solution samples*

1. Sulphate sulphur in solutions containing other easily oxidizable sulphur compounds.
2. Sulphate sulphur in organic solvent phase (amine or phosphate type).
3. Sulphate sulphur in solutions free of other sulphur compounds.
4. Total sulphur in solutions.

B. *Solid samples*

1. Sulphate sulphur.
2. Sulphide sulphur.
3. Total sulphur, free sulphur absent.
4. Total acid soluble sulphur (sulphate sulphur in concentrates for specification purposes).
5. Total sulphur in pyrites.
6. Total sulphur in crude sulphur.

RANGE

This method covers the range 0.01% S and up in solids and 0.01 gm/l S in solutions. Sulphate sulphur in solutions containing other sulphur compounds should not be considered present in significant amounts unless at least 0.05% S is reported.

OUTLINE

A number of methods for the determination of sulphur have been investigated in the Division's laboratory from time to time. With the exception of the combustion method, METHOD S-2 (which is rapid and convenient for small amounts of sulphur if high accuracy is not needed) none has proved as satisfactory for general use as the classical method using precipitation of sulphate with barium chloride.

The precipitation is carried out by adding cold barium chloride solution to the boiling sulphate solution (except in the case of the determination of sulphate sulphur in solutions containing other sulphur compounds air-oxidized to sulphate, as discussed below). This procedure is employed because barium sulphate supersaturates less readily in boiling solution. Barium sulphate is very slightly soluble in dilute mineral acid solutions at room temperature, the solubility being given as 0.4 to 8.7 mg $BaSO_4$ per 100 ml for hydrochloric acid concentrations of 0 to 1.0N (1). The precipitate is notoriously subject to co-precipitation and has been the subject of an enormous amount of research over the years. Most of this work is summarized in the text books (1, 2) and it will suffice here to note that occlusion of sulphates and acid sulphates of metals other than barium corresponds to from 5 to 20 mg of interfering element per gram of barium sulphate, that ferric iron and chromic chromium are serious offenders and that occlusion is generally worse if large amounts of alkali chlorides are present. This occlusion leads to *low* rather than high results because of the decomposition of the acid sulphates of these metals at the ignition temperature used (2) and because the atomic weight of barium is higher than that of most other elements. On the other hand, some barium chloride is always occluded and this gives positive errors. In general the positive and negative errors tend to balance.

Total Sulphur Determination, Solids

In solid samples, sulphur may occur as sulphide, sulphate or free sulphur. The latter is rarely found in ores, but may be present in residues as a result of decomposition of sulphides in auto-oxidation processes, from decomposition of sulphite in sulphurous acid leaching, or from pyrrhotite and certain other sulphides in ordinary acid leaching. (Some minerals liberate part of their sulphur in this form on acid attack.) Crude sulphur, used in sulphuric acid manufacture may also be submitted occasionally for assay.

If total sulphur is requested, any free sulphur and sulphide sulphur must be oxidized to sulphate. Loss of sulphide sulphur will occur if the ore is attacked by acid only, without an oxidizing agent. The oxidation may be carried out in the wet way, using aqua regia, nitric acid and potassium chlorate, or bromine. For ores and residues, however, an oxidizing fusion using a sodium carbonate: potassium nitrate mixture is preferred in most cases, since if lead, barium or strontium are present, insoluble sulphates will be formed during the initial attack if acids are used. These insoluble compounds will then be filtered off with the silica and the sulphur in them lost. During the fusion attack, these compounds are converted to carbonates which are filtered off and the sulphate, which is converted to an alkali sulphate, is recovered in the filtrate. If lead only is present, it is possible to complex it using ammonium chloride (3) and acid attack may be used, but this is not ordinarily considered desirable because of the increase in occlusion errors in precipitation. It should be pointed out however, that occlusion errors are not negligible with the fusion method either.

In the case of pyrites and similar materials used for acid production, a wet attack is satisfactory and somewhat more accurate. In the method given, which is due to Allen and Bishop (4), an additional step is included. This involves reduction of ferric iron to ferrous using aluminum powder, to reduce iron contamination of the precipitate. The precipitation is carried out in cold dilute solution to further reduce such contamination.

Sulphide Sulphur in Solids

In many cases, the sulphide (or sulphate) content of ores must be determined. In this case oxidation is avoided, and the alkaline earth and lead sulphates are converted to carbonates by boiling with sodium carbonate solution (5).

The corresponding carbonates are in all cases more insoluble than the sulphates so the reaction readily proceeds to completion with the result that all the sulphate is taken into solution. It is even stated that it is possible to distinguish lead sulphate, which can be converted with ammonium carbonate, and barium sulphate, which requires the sodium carbonate (6), but this has not been tested here. Using the sodium carbonate treatment the sulphate sulphur is obtained in the filtrate and the sulphides are left behind. This sulphide sulphur in the residue can then be determined by one of the total sulphur procedures e.g. this method, "Procedure" Section B (5), or by the combustion method. Alternatively the sulphate sulphur can be determined in the filtrate, and total sulphur in the original sample, the sulphide sulphur being estimated by difference. The latter procedure is usually more rapid, but the former is preferred if the sulphide content is low.

Table 1

Some Sulphide Minerals Commonly Found in Ores

Mineral	Formula	Solubility in acids
Pyrite	FeS_2	insol. HCl, completely sol. in HNO_3 (most of sulphur oxidizes).
Marcasite	FeS_2	sol. in HNO_3, evolves free sulphur.
Pyrrhotite	Fe_5S_6 to $Fe_{16}S_{17}$	decomp. by HCl, evolves H_2S.
Arsenopyrite	FeS_2 . $FeAs_2$	decomp. by HNO_3, evolves sulphur.
Bornite	Cu_5FeS_4	soluble in HCl, evolves sulphur.
Chalcopyrite	$CuFeS_2$	decomposed by HNO_3, evolves free sulphur.
Chalcocite	Cu_2S	soluble in nitric acid.
Covellite	CuS	
Galena	PbS	decomp. by strong HNO_3 with separation of some sulphur and formation of some $PbSO_4$.
Pentlandite	FeNiS	
Cobaltite	CoS_2 . $CoAs_2$	soluble in warm nitric acid; evolves sulphur.
Sphalerite	ZnS	dissolves in HCl, evolves H_2S.

A separate procedure for the determination of sulphate in concentrates is included, primarily in connection with refinery specifications. At the refinery, the concentrates from the mines are upgraded using tributyl phosphate extraction from nitric acid solution. Sulphate in excessive amounts reduces the efficiency of the process and a limited amount only is permitted. Since this concerns only sulphate that is soluble in nitric acid, the method is designed primarily to determine this.

Sulphate Sulphur in Solutions

If no other sulphur compounds are present, one simply precipitates the sulphate in the usual way, omitting the oxidizing treatment.

Solutions from sulphurous acid leaching, and from auto-oxidation processes, may contain a variety of sulphur-containing ions, other than sulphate, in fairly large amounts. Sulphuric acid and carbonate leach liquors may also contain some of these ions if the ore contains sulphides, although usually only traces are present. Some of these compounds, e.g. dithionate and tetrathionate, are quite stable, do not form insoluble barium compounds, and do not interfere. Others, notably sulphite, thiosulphate, trithionate, pentathionate and hexathionate, all

tend to form some sulphate on standing or as the result of air-oxidation. Sulphite and thiosulphate are stated to form rather insoluble barium salts (although tests conducted in this laboratory showed that if this is the case, these salts are nevertheless soluble in acetic acid). Sulphite can be stabilized (7) by the addition of formaldehyde (5 ml of 40% strength for each 0.01 mole of sulphite). This not only prevents air oxidation, but is remarkably effective in decreasing the interfering effect of iron, and in preventing the interaction of sulphite and thiosulphate to give free sulphur.

$$SO_3^{--} + HCHO + H_2O \longrightarrow HCHO \,.\, HSO_3^- + OH^-$$

$$HSO_3^- + HCHO \longrightarrow HCHO \,.\, HSO_3^-$$

The first reaction is instantaneous, but the second requires about 5 minutes.

Glycerol and mannitol which have been suggested in the early literature (8) for this purpose do not appear to be particularly effective (9).

The addition of iodine to convert thiosulphate to tetrathionate has been proposed by Kurtenacker and Wollak (10), since thiosulphate is strongly co-precipitated by barium sulphate while tetrathionate is not. Oxidation of sulphite is, of course, prevented by prior treatment with formaldehyde.

$$Na_2 SO_3 + I_2 + H_2O \longrightarrow H_2SO_4 + 2\ Na\ I$$

In routine use for solutions in which sulphite predominates, the step is attended by considerable risk and for this reason it is not recommended.

In addition to the treatment with formaldehyde, the barium sulphate is precipitated cold as a further precaution against air-oxidation. As previously noted, this tends to result in increased solubility loss, due to the tendency of barium sulphate to supersaturate in cold solutions. The effect is more than counter-balanced by co-precipitation and air-oxidation of other compounds so that results in general are a few percent high.

This determination should, of course, be carried out as soon as possible after the samples are received.

Occasionally it is necessary to determine the sulphate content of organic solutions used for solvent extraction of uranium and thorium. This is most conveniently done by stripping the sulphate from the organic solution with 10% sodium carbonate solution, and determining the sulphate content of the strip solution. The amines strip readily with one extraction, but phosphate and other phosphorus compounds will require two or more treatments, and may give trouble with third phase formation. A centrifuge can be used to assist phase disengagement if necessary.

Total Sulphur in Solutions

This is carried out by oxidizing all the sulphur compounds to sulphate by boiling with bromine water. Dithionate is not oxidized by most oxidizing agents at room temperature. On boiling in strongly acid solution, however, it decomposes slowly to sulphate and sulphite and the latter is then oxidized by the oxidizer to sulphate. The reaction being continuously displaced, goes to completion. This has not been experimentally proven here, but Back (11) found that in manganese leach solutions containing a mixture of sulphate and dithionate, the total sulphur determined by the usual procedure agreed very closely with the sum of the sulphate and dithionate values. Peterson (12) reports that 5 hours boiling is needed.

APPARATUS

Beakers, Griffin low-form:	50, 100, 250, 400 and 600 ml sizes.
Beakers, Berzelius:	250 and 400 ml sizes.
Flasks, Erlenmeyer:	125 ml or 250 ml size.
Watch glasses:	to fit above beakers.
Funnels, Pyrex, Bunsen filtering, long stem, fluted:	65 mm dia. at top.
Funnel stands:	
Crucibles, alundum, ignition:	
or	
Crucibles, porcelain:	Coors No. 1.
Crucibles, platinum:	30 ml size.
Evaporators, Fisher-Moroney:	
Desiccator:	
Hot plates:	
Ovens:	
Muffles:	
Steam baths or hot water baths:	
Asbestos board, with hole to fit platinum crucible:	

REAGENTS

Hydrochloric acid, concentrated:	
Nitric acid, concentrated:	
Hydrochloric acid, dilute:	1:1 v/v.
Acetic acid, 10%:	v/v.
Barium chloride solution, 10%:	w/v.
Barium chloride solution, 5%:	w/v.
Bromine:	
Bromine water, saturated:	
Bromine-carbon tetrachloride mixture:	2 parts bromine to 3 parts carbon tetrachloride by volume.
Ammonium chloride:	
Potassium chlorate:	
Formaldehyde, 40% solution:	
Methyl red indicator:	
Silver nitrate-nitric acid test solution:	1% $AgNO_3$ in N nitric acid.

Sodium carbonate fusion mixture: 12 parts sodium carbonate to 1 part potassium nitrate, by weight.

Methyl alcohol:

Sodium carbonate solution, 1%:

Aluminum powder; C.P.:

Filter papers: Whatman No. 30
Whatman No. 42.

PROCEDURE

A. Solution Samples

1. *Sulphate Sulphur in Solutions Containing Other Easily Oxidizable Sulphur Compounds*

Pipette a suitable aliquot (0.01 to 0.05 gm S) into a 400-ml beaker. If the solution is alkaline, cautiously neutralize to the pink colour of methyl red using dilute (1:1 v/v) hydrochloric acid. Adjust the volume to about 200 ml. Add 5 ml of 40% formaldehyde for each 0.01 mole of sulphite (20 ml will suffice for a 25-ml aliquot of saturated sulphurous acid solution), and let stand 10 minutes. Now add 20 ml of 10% acetic acid solution, and then with constant stirring add a slight excess of 10% barium chloride solution (1 ml for each 0.01 gm S). Let stand at room temperature 1 hour. Decant as much as possible of the supernatant solution into a clean beaker. To the precipitate, add about 50 ml of water, 1 ml of concentrated hydrochloric acid, and 1 ml of 10% barium chloride solution. Stir, let settle, and decant again. Once more add 50 ml water, 1 ml hydrochloric acid and 1 ml of 10% barium chloride, and digest for 15 to 30 minutes on the hot plate. Filter through a Whatman No. 42 filter paper, receiving the filtrate in the beaker containing the combined supernatant solutions. Test the first portion of the filtrate for complete precipitation by adding a few drops of barium chloride solution. Transfer the precipitate completely to the filter paper and wash well with cold water (eight to ten times). Place the folded paper in a tared ignited crucible. Dry, and burn off the paper over a low flame. Transfer to a muffle and ignite at 900°C for 30 minutes. Cool and weigh. Record the weight of barium sulphate and calculate as sulphur.

2. *Sulphate Sulphur in Organic Solvent Phase (Amine or Phosphate Type)*

Pipette 50 ml of the solvent into a 50-ml separatory funnel and shake for 1 minute with 50 ml of 10% aqueous sodium carbonate solution. Repeat the extraction with two 10-ml portions of the carbonate solution, combine the extracts and transfer to a 100-ml volumetric flask. Make to the mark, mix well and continue as in subsection 3 below. If a new solvent is being analyzed for the first time, verify that complete stripping has been obtained by repeating the above stripping procedure, and determining the sulphate content of the second strip solution separately.

3. *Sulphate Sulphur in Solutions Free of Other Sulphur Compounds*

Pipette a suitable sample (0.01 to 0.05 gm S) into a 400-ml beaker. Add a few drops of methyl red indicator and if the solution is coloured yellow, cautiously adjust to pink using dilute hydrochloric acid. Adjust the volume of the solution to 200 ml. Add 10 ml dilute (1:1 v/v) hydrochloric acid and bring to a boil. With constant stirring add 10% barium chloride in slight excess (1 ml for each 0.01 gm S). Stir well and digest just below boiling (at about 90° C) for an hour or more—preferably overnight. Decant the supernatant solution into a clean beaker. Add about 50 ml of water, 1 ml of hydrochloric acid and 1 ml of 10% barium chloride solution to the precipitate, and digest for 30 minutes on the hot plate.

Filter through a Whatman No. 42 paper into the beaker containing the decanted supernatant solution and test the first portion of filtrate with a few drops of barium chloride solution. Wash with warm water in small portions until the filtrate no longer gives a test for chloride with silver nitrate-nitric acid solution. Transfer the paper to a tared ignited crucible. Dry and cautiously burn off the paper over a low gas flame. Place the crucible in a muffle at 900° C for 30 minutes. Cool in a desiccator and weigh. Record the weight of barium sulphate and calculate as sulphur.

4. *Total Sulphur in Solutions*

Place 25-50 ml saturated bromine water into a 125-ml Erlenmeyer flask (250-ml size if dithionate is present). Add a suitable volume of sample (0.01 to 0.05 gm S) by pipette. Mix and let stand without heating for 20 minutes, adding more bromine water if no bromine colour is visible. Boil until the bromine colour becomes faint, then add 5 ml of hydrochloric acid. If dithionate may be present, add a further 25 ml of saturated bromine water and boil for at least 5 hours adding water if necessary to maintain the volume. Otherwise, boil until all the bromine is expelled.

Transfer the solution to a 400-ml beaker, filtering if necessary, and dilute to 200 ml. Precipitate and weigh the barium sulphate as described in procedure A(3), above. Record the weight and calculate as sulphur.

B. Solid Samples

1. *Sulphate Sulphur*

Weigh a suitable sample, (up to 5 gm) containing 0.01 to 0.05 gm S, into a 250-ml beaker. Add about 5 gm sodium carbonate, insert a stirring rod or anti-bumping device (or use a Moroney evaporator) and boil for 20 minutes. Filter through a Whatman No. 42 paper into a 400-ml beaker and wash well with hot water. Reserve the residue for procedure B(2). To the filtrate, add a few drops of methyl red indicator, cautiously neutralize with hydrochloric acid, then add a 5 ml excess of the acid. Boil to eliminate carbon dioxide and dilute to 200 ml. Finally boil again and complete the determination as outlined in procedure A(3). Record the weight of barium sulphate obtained and calculate as sulphur.

2. *Sulphide Sulphur*

(a) Sulphide Content High

Carefully dry the residue from the carbonate treatment in procedure B(1) by washing first with alcohol, then drying in an oven at 70° C. Cool in a desiccator, transfer as completely as possible to a tared beaker and weigh. Record the weight obtained, then carry out a total sulphur determination on a suitable portion of the material using either procedure B(3), or procedure B(5). From the sample and residue weights, and the weight of the portion taken for the total sulphur determination, calculate the sulphide sulphur as sulphur.

(b) Sulphide Content Low

Carefully dry the residue from the carbonate treatment in procedure B(1) by washing first with alcohol then drying in an oven at 70° C. Cool in a desiccator, transfer to a tared beaker as completely as possible, and weigh. Record the weight obtained, then carry out a total sulphur determination by the

combustion method (METHOD S-2). From the sample and residue weights and the weight of the portion taken for the combustion sulphur determination, calculate the sulphide content as sulphur.

3. *Total Sulphur*

(a) Free Sulphur Absent

Weigh a suitable sample (0.2 to 2 gm) containing 0.01 to 0.05 gm S, into a platinum crucible and mix thoroughly with about five times its weight of fusion mixture (12 parts sodium carbonate: 1 part potassium nitrate). Set the crucible in a hole in a piece of asbestos board and heat gently, at first, over a gas burner. Finally raise the heat so that the sample is completely decomposed.

Let cool and transfer the crucible and its contents to a 400-ml beaker. Add 50-100 ml distilled water and digest on a padded hot plate until the mass is thoroughly disintegrated. Add a drop or two of alcohol to reduce manganates, filter and wash the residue with hot 1% sodium carbonate solution.

Add a drop or two of methyl red to the filtrate, neutralize cautiously with hydrochloric acid, and add 10 ml in excess. Evaporate to dryness. Add a further 10 ml of concentrated hydrochloric acid, take to dryness again and bake at 100° C to dehydrate the silica (preferably overnight).

Cool the beaker and add 5 ml of hydrochloric acid followed by 50 ml of water. Digest on a padded hot plate until the soluble salts are dissolved. Filter on a Whatman No. 30 filter paper into a 400-ml beaker and wash the residue thoroughly using boiling water in small portions.

Dilute the filtrate to about 200 ml, heat to boiling and complete the determination as outlined in procedure A(3). Record the weight of barium sulphate obtained and calculate as sulphur.

(b) Free Sulphur Absent (Alternative Procedure)

Weigh a suitable sample (0.5 to 2 gm) containing 0.01 to 0.05 gm S into a 250-ml beaker. If the sample is high in sulphide, add 15 ml water.

Add 15 ml nitric acid, and cover with a watch glass, let any reaction subside and let cool. Then add about 2 gm of solid potassium chlorate and swirl to mix. Let stand at room temperature for 15 minutes or more. Evaporate to small volume, and then let cool. Rinse the cover and the sides of the beaker with water, add 5 ml of hydrochloric acid and evaporate to dryness. Bake on a hot plate at moderate heat for 30 to 45 minutes.

Cool, add 5 ml hydrochloric acid and let stand for a few minutes. Rinse down the cover and sides, and add about 20 ml water. If there is a residue proceed according to (i) below if its composition is unknown, or according to (ii) if it is known to contain no barium or strontium.

(i) *Treatment of Residue (composition unknown)*—Boil for a few minutes and filter through a Whatman No. 30 filter paper into a 400-ml beaker (not etched or badly scratched) and wash the residue well with boiling water. Reserve the filtrate.

Transfer the paper and residue to a platinum crucible. Dry and ignite at a low temperature over a burner using an asbestos shield. Fuse the residue remaining with five times its weight of fusion mixture (sodium carbonate 12 parts: potassium nitrate 1 part) as in the previous procedure. Cool, transfer the crucible to a 400-ml beaker and add 50-100 ml distilled water. Digest on a padded hot plate until the mass is thoroughly disintegrated. Filter and wash the residue with hot 1% sodium carbonate solution. Discard the residue. Combine

the filtrates, carefully avoiding loss by effervescence, add a few drops of methyl red indicator and add additional hydrochloric acid to neutralize carbonate if necessary. Evaporate the combined filtrates to dryness to dehydrate silica. Bake at 100°C for several hours. Cool the beaker and add 5 ml of hydrochloric acid followed by 50 ml of water. Digest on a padded hot plate until the soluble salts are dissolved. Filter on a Whatman No. 30 filter paper into a 400-ml beaker and wash the residue thoroughly using hot water in small portions.

Dilute the filtrate to about 200 ml, heat to boiling and complete the determination as outlined in procedure A(3). Record the weight of barium sulphate obtained and calculate as sulphur.

(ii) *Treatment of Residue (if Free of Barium or Strontium)*—If lead is the only element present which is likely to tie up sulphate, add at this point 5 gm ammonium chloride. Boil for a few minutes and filter through a Whatman No. 30 filter paper into a 400-ml beaker. Wash the residue well with hot water.

Adjust the volume to about 200 ml and heat to boiling. Complete the determination as outlined in procedure A(3). Record the weight of barium sulphate obtained and calculate as sulphur.

4. *Total Acid Soluble Sulphur ("Sulphate" Sulphur in Concentrates for Specification Purposes)*

Weigh a 2.000-gm sample and transfer it to a 150-ml beaker. Moisten the sample with water. Add 25 ml of nitric acid, heat on a steam bath until the reaction ceases, and evaporate to dryness. Add 5 ml of dilute (1:1,v/v) hydrochloric acid and 50 ml of water; warm to dissolve all soluble matter. Filter the sample while hot through a Whatman No. 42 filter paper into a 400-ml beaker. Wash the paper and residue thoroughly with hot water. Heat the solution to boiling and complete the determination as outlined in procedure A(3). Record the weight of barium sulphate and calculate as sulphur, (or, for comparison purposes in connection with umpire determinations, calculate as sulphate).

5. *Total Sulphur in Pyrites*

Weigh a suitable sample (0.01 to 0.05 gm S) into a dry 250-ml beaker, add 5 ml of bromine-carbon tetrachloride mixture (2 parts bromine : 3 parts carbon tetrachloride by volume). *Caution:* wear safety glasses and work in a well-ventilated hood. Cover with a watch glass, swirl to mix, and let stand 10 minutes.

Transfer the beaker to a hot water bath and let stand (at about 90°C) until the reaction has stopped. Remove the watch glass and let the solution evaporate to dryness. Moisten the residue with about 10 ml of concentrated hydrochloric acid, evaporate to dryness and bake for an hour or more at 100°C. Take up the residue in 2 ml of hydrochloric acid followed by 50 ml of water. Rinse down the watch glass and the sides of the beaker, transfer to a hot plate and bring to a boil. Boil for about 10 minutes, let cool and add 0.2 gm aluminum powder. Stir until the solution is decolorized and filter into a 600-ml beaker, washing well with several small portions of hot water. Dilute to 400 ml and add 2 ml of concentrated hydrochloric acid. Precipitate the sulphate in the cold by adding 50 ml of 5% barium chloride solution dropwise with stirring at a rate not exceeding 5 ml per minute. Let the precipitate settle 2 hours, or better, overnight. Filter on a Whatman No. 42 filter paper, receiving the filtrate in a clean beaker.

Test the first portion for complete precipitation with a few drops of barium chloride solution. Wash with small portions of hot water until the washings give no test for chloride with silver nitrate-nitric acid test solution. Place the folded paper containing the precipitate in a tared ignited crucible. Dry, and burn off the paper over a low flame. Transfer to a muffle and ignite at 900°C for 30 minutes. Cool and weigh. Record the weight of barium sulphate and calculate as sulphur.

6. *Total Sulphur in Crude Sulphur*

Weigh 0.2 to 2 gm into a 500-ml Berzelius beaker. Add 15 ml of the bromine: carbon tetrachloride mixture (2 parts bromine: 3 parts carbon tetrachloride by volume). *Caution:* wear safety glasses, carry out in a well-ventilated hood. Cover with a watch glass, swirl to mix and let stand for 10 minutes.

Add 100 ml water containing 1 gm sodium carbonate and boil, adding water to keep the volume up to about 100 ml. When the bromine colour becomes faint, add 5 ml of hydrochloric acid and continue boiling to expel the bromine. Filter if necessary. Heat the solution to boiling, precipitate the barium sulphate and complete the determination as outlined in procedure A(3). Record the weight of barium sulphate obtained and calculate as sulphur.

CALCULATIONS

$$\% \text{ S} = \frac{\text{wt. } BaSO_4 \text{ (gm)} \times 0.1374 \times 100}{\text{sample weight, (gm)}}$$

$$\text{gm/l S} = \frac{\text{wt. } BaSO_4 \text{ (gm)} \times 0.1374 \times 1000}{\text{vol. sample taken, (ml)}}$$

$\%$ SO_4 (required for precipitates only for umpire purposes)

$$= \frac{\text{wt. } BaSO_4 \text{ (gm)} \times 0.4115 \times 100}{\text{sample wt., (gm)}}$$

If no weighable precipitate is obtained, report the result as the minimum amount detectable, an actual figure based on the sample weight and volume taken. Assuming such a precipitate would amount to less than 1 milligram report

$$\% \text{ S} = \frac{\text{less than } 0.001 \times 0.1374 \times 100}{\text{sample wt., (gm)}}$$

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The Determination of Sulphur in Ores, Combustion Method

METHOD S-2

SCOPE

This is a rapid method for the determination of sulphur in ores, without regard to the form in which it may be present.

RANGE

The method is suitable for sulphur contents in the range 0.01% to 5% S. Higher percentages may be determined with a corresponding decrease in accuracy.

OUTLINE

When an ore containing sulphur is ignited at a temperature of 2600° F, in a stream of oxygen, sulphur is evolved as sulphur dioxide and sulphur trioxide. If these gases are passed through a glass bubbler and are absorbed in a solution of weak hydrochloric acid containing starch and potassium iodide, sulphur can be determined by titration of the absorbing solution. This solution is titrated with potassium iodate, the potassium iodate liberating iodine as fast as it is used up by the sulphur dioxide, and the sulphur is calculated on the basis of the amount of potassium iodate used. The sulphur equivalent is based upon the reactions

(1) $KIO_3 + 5\ KI + HCl \longrightarrow 3\ I_2 + 6\ KCl + 3\ H_2O$

(2) $SO_2 + I_2 + 2\ H_2O \longrightarrow H_2SO_4 + 2\ HI$

Recovery is not quantitative, but has been found to be consistently about 93% of the total sulphur present. Percentage sulphur is calculated by means of a factor determined from standard samples, using potassium iodate solution made up on the basis of 93% recovery. This is done as follows:

In a solution containing 0.225 gm KIO_3 per litre, 1 ml KIO_3 is theoretically equivalent to 0.1 mg sulphur, assuming quantitative conversion.

On the basis of 93% conversion of sulphur to sulphur dioxide used, this would give:

$$0.225\ \text{gm} \times 0.93 = 0.2069\ \text{gm of } KIO_3 \text{ per litre.}$$

Then 1 ml KIO_3 solution containing 0.2069 gm KIO_3 per litre is equivalent to 0.1 mg sulphur.

A solution factor is established by each analyst for both strong and weak KIO_3 solutions using the standard samples provided for this purpose. This factor calculated as "grams of sulphur per ml", includes the volumetric factor and the recovery factor. The two titrating solutions should be equivalent to approximately 1.0 mg sulphur per ml and 0.1 mg sulphur per ml respectively. The use of solutions of these strengths has been found to simplify the choice of a suitable sample weight and the estimation of the approximate titration required.

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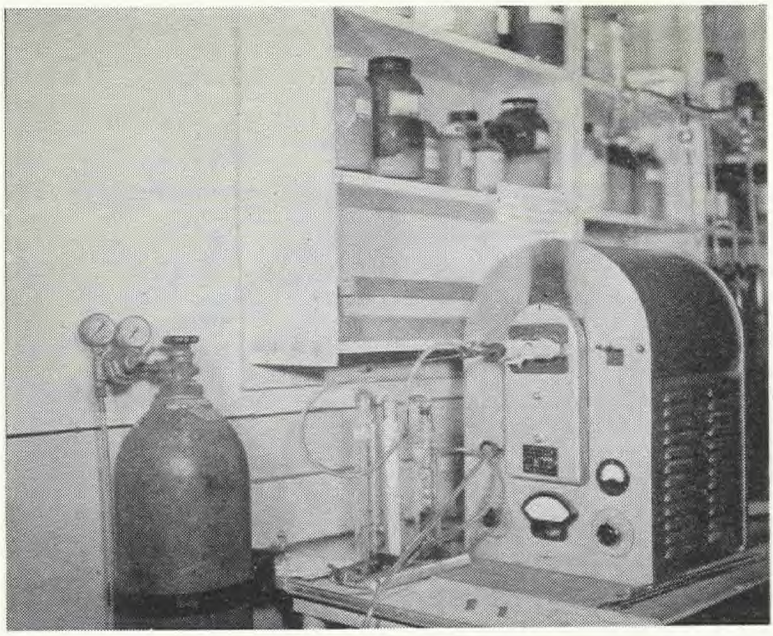
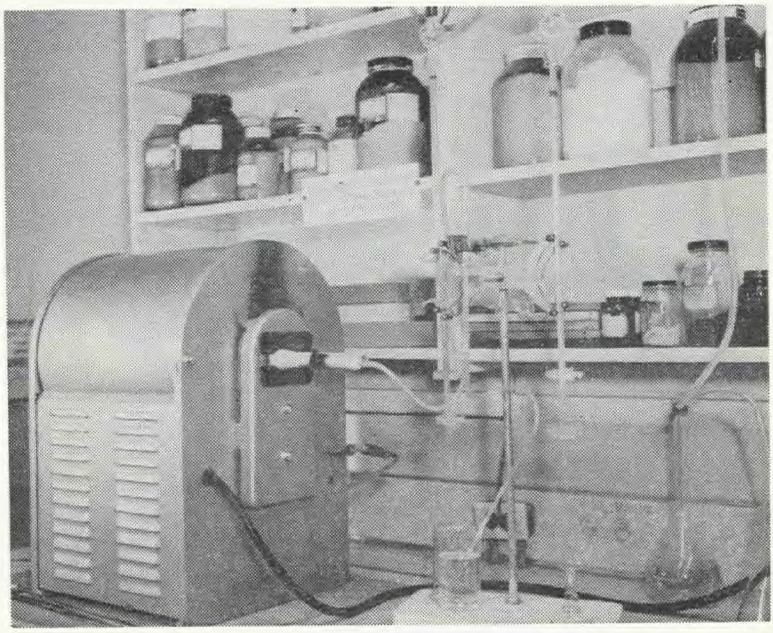


A.



B.

FIG. 1—COMBUSTION APPARATUS FOR SULPHUR DETERMINATION. A. FRONT VIEW, SHOWING PURIFYING TRAIN. B. REAR VIEW, SHOWING FUME TRAP AND TITRATION SET-UP.

Interferences

Large amounts of fluorine may cause trouble by attacking the combustion boat. Moderate amounts of arsenic give no trouble, although large amounts (over 15%) appear to cause slightly low results.

APPARATUS

See Figure 1 for photographs of complete set-up.

Combustion furnace:	Dietert No. 34410 (reference 3).
Combustion tube:	Dietert No. 3226-17, narrow mouth.
Tube liners:	Dietert type F2 No. 3057.
or	
Boat shields:	Dietert No. 3632.
Combustion boats:	Dietert No. 3031 type D (preignited several hours at 900° C) or Leco Combax Size A.
Fume or dust trap:	Straight form drying tube 100 mm size, packed with glass wool.
Titrating vessel:	Bottom portion of 250 ml Pyrex glass washing bottle or tall form beaker.
Gas dispersing tube:	Fritted glass, extra coarse Fisher 11-137 or Inlet aeration tube Scientific Glass C5362. Note: leave standing in 15% HCl when apparatus not in use.
Storage bottles:	Two 8 litre bottles for KIO_3. One 12 litre bottle for HCl.
Heat deflector:	Dietert 3452.
Boat pusher:	Dietert 3453.
Oxygen purifying train:	Dietert No. 3004 or Leco (part of Scientific Glass No. C7060, No. C7115).
Balance:	Accuracy of $\pm$ 0.05 mg is required.
Burettes:	5 ml micro burettes sim. to Fisher 20-109.
Assembly:	(*See* Figure 1). The fume or dust trap is connected to the exit end of the combustion tube with a rubber stopper and to the aeration tube by a length of Tygon tubing. A stopcock placed between the fume trap and the aeration tube or bubbler is useful in controlling suck back.

REAGENTS

Oxygen:	Oxygen is supplied from the regular 220 cu ft cylinder equipped with a 2-stage reducing valve, at a flow rate of 1500 ml per minute.
Accelerator:	Metallic tin 30 mesh.
Potassium iodate titrating solution, strong:	Dissolve 2.069 gm KIO_3 for each litre of final solution, in water, and make to volume. One ml of this solution is equivalent to 1 mg of sulphur.
weak:	Dilute a suitable volume of the strong solution ten times. 1 ml = 0.1 mg sulphur. Use for samples containing less than 0.10% sulphur.
Starch-iodide solution:	Add 3 gm starch to 5-10 ml cold water and make into a paste. Pour the paste into 250 ml of boiling water, cool, add 10 gm KI and stir until the KI is in solution. Dilute to 500 ml.
HCl solution, 1.5%:	30 ml HCl made up to 2000 ml with distilled water.
Standard Ore Sample:	Prepare several pounds of typical ore and standardize carefully by METHOD S-1. Use this ore in establishing the titer of the iodate solution.

PROCEDURE

Make sure that the temperature of the furnace is 2600° F and that it is maintained at this value during the determination. Weigh an appropriate amount of dry ore (selected from the Table at the end of this procedure) into a boat, and spread the sample well. Cover with roughly twice the weight of metallic tin as was taken for the sample and place a shield over the boat. (Use of a shield may not be necessary if a combustion tube liner is in use.) Add 125 ml of 1.5% HCl and 4 ml of starch-iodide solution to the titrating vessel. This is the absorbing solution. Connect the dust trap and aeration tube to the exit end of the combustion tube. Place the aeration tube in the absorbing solution and then insert the rubber stopper containing the heat deflector in the front end of the combustion tube. Pass oxygen into the absorbing solution for about 30 seconds at 1500 ml per minute to clean out the tube. Titrate the solution to a distinct blue end-point. Take a reading on the burette. Remove the deflector and cautiously place the boat in the furnace, pushing the boat into the position of maximum heat with the boat pusher. Insert the deflector and preheat the sample for 1 minute with the oxygen supply shut off. Then turn on the oxygen and adjust the flow rate to about 1500 ml per minute.

Titrate with the iodate solution to restore the blue colour as it is removed by the absorption of SO_2 in the absorption solution. Continue titrating until there is no further decolouration of the solution while bubbling is continued for 3-4 minutes, and adjust to the same shade as was taken for the initial end-point. Record the burette reading.

Carry out a blank determination in exactly the same way, with each set of determinations, using a boat containing accelerator but no sample. Run samples in duplicate, and correct the differences in the burette readings for the blank.

Table of Suggested Sample Weights

% Sulphur Present	*Suggested Sample Weight*	*Titrate With*
<0.10	1.0 gm	weak KIO_3 solution
0.1–0.2	1.0 gm	strong KIO_3 solution
0.2–1.0	0.5 gm	strong KIO_3 solution
1.0–2.0	0.25 gm	strong KIO_3 solution
2.0–5.0	0.10 gm	strong KIO_3 solution
5.0–10.0	0.05 gm	strong KIO_3 solution

CALCULATIONS

$$\% \text{ Total Sulphur} = (\text{diff. in burette reading}) \times \text{sol'n factor} \times \frac{100}{\text{sample weight gm}}$$

If the sample gives approximately the same reading as the blank, the amount of sulphur present should be reported as less than the minimum amount detectable (an actual figure based on the sample weight and volumes used) rather than using the term "not detected". The minimum amount detectable may be taken as equivalent to a titration difference of 0.02 ml and the figure to report may be calculated on this basis, i.e.

$$\% \text{ S} = \text{less than } 0.02 \times \text{factor} \times \frac{100}{\text{sample wt. gm}}$$

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The Gravimetric Determination of Silica in Ores and Mill Products

METHOD Si-1

SCOPE

The methods given below are applicable to all ores or mill products which contain silica in amounts large enough to be determined gravimetrically.

RANGE

Silica from 0.5 to 2 percent can be determined with an accuracy of 5 percent. Larger amounts can be determined with greater accuracy.

OUTLINE

The determination of silica described here is based on the classical procedure (1, 2, 3) whereby the silica in the solution from the sample is dehydrated with hydrochloric or perchloric acid and filtered, dried, and weighed as an impure silica precipitate. The silica in the impure precipitate is then volatilized with hydrofluoric acid, and the impurities which remain behind are weighed and the silica content determined by difference.

The steps of the procedure are covered in a wealth of detail by Hillebrand *et al.*, (1) and it will suffice here to note some of the important features only.

Fluorine, which is present in many uranium ores, causes losses in the initial attack, since silicon tetrafluoride is evolved on boiling with strong acids.

$$2H_2SO_4 + 2\ CaF_2 + SiO_2 \longrightarrow SiF_4 + 2\ CaSO_4 + 2H_2O$$

The loss is not quantitatively related to the fluoride content and can often be overcome by keeping the beaker covered during the initial digestion, since moisture will tend to hydrolyze the silicon tetrafluoride.

$$2H_2O + SiF_4 \longrightarrow 4HF + SiO_2$$

If the fluoride content is above 1%, the use of boric acid in the perchloric acid causes its volatilization before significant loss of silicon can occur (4).

$$H_3BO_3 + 3HF \longrightarrow BF_3 + 3H_2O.$$

Any fluoride that remains is complexed as HBF_4, and is less likely to react with silica.

The boron left in solution is carried down by the silica when it precipitates, and since it will volatilize with the hydrofluoric acid used to volatilize silica, it would constitute an interference. This is avoided by volatilizing it as the trimethyl compound in the presence of sulphuric acid

$$H_3BO_3 + 3CH_3OH \longrightarrow B(OCH_3)_3 + 3H_2O$$

APPARATUS

Beakers, Pyrex, Griffin low form:	250 ml size.
Watch glasses:	
Funnels, Bunsen filtering, long stem:	
Platinum crucibles: (with covers)	30 ml and 50 ml.
Desiccators:	
Filter support:	
Filter paper:	Whatman No. 42, 9 cm.
Analytical balance:	
Muffle furnace:	
Gas burners:	
Perchloric acid fume hood:	
Safety glasses:	

REAGENTS

Nitric acid, concentrated:	
Sulphuric acid, concentrated:	
Hydrochloric acid, concentrated:	
Hydrochloric acid, dil.:	1:1, v/v.
Perchloric acid, concentrated:	70%.
Perchloric acid, dil.:	20%, — 140 ml 70% acid diluted to 500 ml.
Perchloric acid, dil, saturated with boric acid at 50° C:	
Perchloric acid wash solution:	5%, — 35 ml 70% acid diluted to 500 ml.
Hydrofluoric acid:	
Ammonium hydroxide, dil.:	1:1, v/v.
Sulphuric acid, dil:	1:1, v/v.
Ammonium chloride:	
Boric acid:	
Sodium carbonate:	
Sodium nitrate:	
Methyl alcohol, absolute:	

PROCEDURE

A. For Ores and Solids

(1) *Sulphide Ores*

Weigh a portion of the ore into a 250-ml beaker. Add 10-15 ml of water and 10-15 ml of nitric acid. Heat gently until strong action has ceased and evaporate to dryness. Cool, and wash down the sides of the beaker with distilled water. Add 5 ml of concentrated nitric acid, evaporate to dryness and bake at 110°C for 1-2 hours. Cool, add 20-25 ml of 1:1 hydrochloric acid and 1-2 gm of

ammonium chloride. Digest until the soluble salts are in solution and filter through a No. 42 Whatman filter paper. Wash the residue and paper a few times, first with hot 1:1 hydrochloric acid and then with hot water. If silver or tungsten are present, give the residue a third wash with warm 1:1 ammonium hydroxide followed again by hot water. Examine the residue for undecomposed silicates. Transfer the residue and paper to a platinum crucible, add 5-6 drops of 1:1 sulphuric acid, dry and burn off the filter paper at as low a heat as possible. If the amount of residue is small and it does not contain large amounts of undecomposed silicates, proceed as follows: Ignite the residue in a muffle, cool in a desiccator and weigh. Cover the residue in the platinum crucible with 8-10 drops of 1:1 sulphuric acid and 4-5 ml of hydrofluoric acid. Evaporate the mixture to complete dryness. If there is a residue, repeat the sulphuric and hydrofluoric acid treatment a few times. Heat gently over a burner until all sulphuric acid is expelled and then ignite in a muffle at 950°C, cool in a desiccator and weigh. The loss in weight represents the amount of silica as SiO_2. If tungsten is present the ignition temperatures should be below 850°C.

If the residue from the acid digestion is large or contains undecomposed silicates, fuse with sodium carbonate and treat as given under subsection 3, below.

2. *Ores and Mill Products in General*

Weigh a portion of the ore into a 250-ml beaker, add 20-30 ml of distilled water and 15-20 ml of 20% perchloric acid. If the sample contains over 1% fluorine, the perchloric acid should be saturated with boric acid at 50°C. Heat to strong fumes of perchloric and fume for 10-15 minutes. Wash down the sides of the beaker with a little distilled water, heat to strong fumes of perchloric acid and fume again for 5-6 minutes. Dilute to about 75 ml with distilled water, heat to boiling and boil for 5-10 minutes. Filter through a No. 42 paper, wash a few times with warm 5% perchloric acid and then with hot water. Next, wash the residue and paper with hot 1:1 hydrochloric acid and again with hot water. If the sample contains silver or tungsten, re-wash the washed residue with warm ammonium hydroxide and then with distilled water. Examine the residue for undecomposed silicates and transfer the residue and paper to a platinum crucible. Add 5-6 drops of sulphuric acid, dry and burn off the paper at as low a temperature as possible. If perchloric acid saturated with boric acid was used in dehydrating the silica, moisten the residue with 6-8 drops of 1:1 sulphuric acid, add 5-6 ml of methyl alcohol and evaporate to complete dryness. If the amount of residue is small and undecomposed silicates are absent, ignite the residue in a muffle at 950°C, cool in a desiccator and weigh. Volatilize the silica with hydrofluoric acid, ignite and weigh as described in subsection 1, above. If the amount of residue is large and undecomposed silicates are present, proceed as in subsection 3, which follows.

3. *Siliceous Ores and Residues from Acid Digestion*

Mix the ignited insoluble residue from the acid digestion, or 0.5 gm of the ore, in a platinum crucible with about 4-5 gm of sodium carbonate and about 0.1 gm of sodium nitrate. Heat the mixture over a burner at a low heat to expel moisture. Cover the crucible with a platinum cover and raise the heat gradually until a quiet fusion is obtained. Cool, place the crucible and lid in a 250-ml beaker, and add 30-50 ml of water and 15-20 ml of 20% perchloric acid. If the ore contains fluorine the perchloric acid should be saturated with boric acid at 50° C. Digest until the melt dissolves or disintegrates. Remove and wash the

crucible and lid with 5% perchloric acid to remove any adhering particles. Evaporate to strong fumes of perchloric acid and fume for 5-10 minutes. Wash down the sides of the beaker, heat to strong fumes and fume again for 5-10 minutes. *Do not* fume off all the liquid to produce a paste. Dilute to 75 ml with distilled water, heat to boiling and boil for 15-20 minutes. Filter through a No. 42 Whatman filter paper and wash the residue and paper first with warm 5% perchloric and then with distilled water. Next wash the residue and paper with hot 1:1 hydrochloric acid and then with water. Reserve this residue. Add 5 ml of 70% perchloric acid to the filtrate and evaporate to heavy fumes of perchloric acid. Fume for 10-15 minutes, dilute the solution to 75 ml and heat to boiling. Boil for 10 minutes, filter through a new filter paper and wash the residue and paper as before. Transfer both filter papers to a platinum crucible, add 6-8 drops of 1:1 sulphuric acid, dry and burn off the filter paper at as low a heat as possible. If the perchloric acid was saturated with boric acid, add 6-8 drops of 1:1 sulphuric acid and 5-6 ml of methyl alcohol to the residue in the crucible and evaporate to complete dryness. Ignite the crucible in a muffle, cool in a desiccator and weigh. Moisten the weighed residue with 6-8 drops of sulphuric acid and 4-5 ml of hydrofluoric acid. Evaporate to complete dryness, ignite and weigh. If the amount of residue is large, repeat the hydrofluoric acid treatment a few times before igniting and weighing. The loss in weight represents the amount of silica (SiO_2) present.

B. For Solutions ("Soluble" Silica)

Pipette an aliquot portion of the solution into a 250-ml beaker and add 15 ml of 20% perchloric acid.

Evaporate to heavy fumes of perchloric acid and fume for 10-15 minutes. If the solution contains over 1 gm/l of fluorine the perchloric acid should be saturated with boric acid at 50° C. Wash down the sides of the beaker with water, heat to strong fumes of perchloric acid and fume for 5-10 minutes. Dilute to 75 ml with distilled water, heat to boiling and boil for 10-15 minutes. Filter, wash and treat the residue as for siliceous ores (Section A.3).

CALCULATIONS

$$\% \, SiO_2 = \frac{\text{Loss in weight of residue}}{\text{wt. sample}} \times 100$$

$$\text{gm/l } SiO_2 = \frac{\text{Loss in weight of residue}}{\text{aliquot, ml.}} \times 1000$$

If no weighable precipitate is obtained, report the result as less than the minimum amount detectable based on the sample weight or volume taken. Assuming such a precipitate would amount to less than 2 milligrams, report

$$\% \, SiO_2 = \text{less than } \frac{0.002 \times 100}{\text{wt. of sample taken}}$$

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The Colorimetric Determination of Silica

METHOD Si-2

SCOPE

This method is intended for determining small amounts of silica in leach solutions and in certain solid samples, such as high-grade precipitates, gypsum cake and soda ash.

RANGE

The lower limit of the procedure outlined is 0.002 gm/l.

OUTLINE

The reaction of silica with molybdic acid to form molybdisilicic acid is the only known reaction for the colorimetric determination of silicon. The reduction of this compound to the heteropoly blue complex provides the basis for the present method. Molybdisilicic acid can be reduced at higher pH than either molybdiphosphoric or molybdiarsenic acids and by proper pH control only the silica compound is reduced.

The composition of the heteropoly blue compound has been discussed in connection with the arsenic method and the discussion will not be repeated here. Maximum absorbance occurs at 815 mμ and the colour is stable for 12 hours or more.

Since silica is insoluble in the common acids, and is easily dehydrated to the insoluble polymer by heating, addition of hydrofluoric acid is employed to "activate" it

$$HF + \text{polysilicate} \longrightarrow H_2SiF_6 + H_2O$$

It is of course important that no silica be lost as SiF_4 and this is insured by using dilute solutions. The fluoride is destroyed by means of boric acid, reliberating the silica as unpolymerized silicate which then reacts with molybdic acid before it has time to polymerize.

$$2H_2SiF_6 + 3H_2BO_3^- + 4OH^- \longrightarrow 2SiO_3^= + 3BF_4^- + 7H_2O$$

$$SiO_3^= + 12MoO_4^= + 22H^+ \longrightarrow Si\,(Mo_3O_{10})_4^{-4} + 11\,H_2O$$

The molybdisilicic acid is reduced by means of the 1-amino-2-naphthol-4-sulphonic acid-sulphite reagent,

$$Si\,(Mo_3O_{10})^{-4} + HSO_3 \longrightarrow \text{heteropoly blue.}$$

Pentavalent arsenic and phosphorus give colours under similar conditions to that of silica. As we have seen, pH control reduces this interference, and the molybdiarsenic and molybdiphosphoric acids are, in addition, broken up by use of oxalic acid.

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Aluminum, zinc, copper, manganese, calcium, nickel, magnesium, cadmium and ferrous iron do not interfere in concentrations up to 500 times the silica content. Lead, titanium and ferric iron must not be present at concentrations more than 100 times the silica content (4). Ferric iron interferes mainly by consuming reducing agent.

Zirconium and beryllium do not interfere.

Of the anions, oxalate and tartrate must not be present at more than 500 times the silica concentration prior to reduction.

Oxidizing agents such as chromate, nitrate, nitrite and peroxide must be absent since they bleach the blue colour. Peroxide reacts with molybdic acid to give a yellow colour. High concentrations of alkali halides, nitrates and sulphates must be avoided.

Silica contamination is also a serious factor, calling for special search for "silica-free" reagents. These should be reserved for this determination. Plastic containers should be used whenever possible.

APPARATUS

Beakers, Griffin low form:	250 ml and 100 ml sizes.
Platinum crucible:	25 ml.
Funnels, Bunsen filtering, long-stem:	65 mm dia.
Platinum or polyethylene dishes:	100 ml.
Flasks, volumetric:	50, 100, 250 ml.
Pipettes, volumetric:	1, 2, 3, 4, 5, 10, 25 ml sizes.
Nessler tubes, 100 ml tall form:	
Nessler tube rack:	
Clock, interval timer:	
Bottles, reagent, polyethylene:	500 ml sizes.
Spectrophotometer:	
Spectrophotometer cells:	1 cm and 5 cm (clean regularly with ammonia to remove the heteropoly blue stains).

REAGENTS

Hydrochloric acid:	
Hydrochloric acid, dil:	1:1 (v/v).
Sodium carbonate:	silica-free.
Sodium hydroxide:	50% solution, reagent grade, in polyethylene bottles, silica-free.
Hydrofluoric acid solution, dil:	Dilute 1 ml concentrated HF (40%) to 2000 ml in a plastic bottle.
Sodium borate-boric acid buffer:	Dissolve 6.5 gm boric acid in 500 ml water. Adjust pH to 8.5 using reagent, silica-free, 50% sodium hydroxide solution, and dilute hydrochloric acid 1:1 (v/v) solution.
Ammonium molybdate solution:	Dissolve 50 gm $(NH_4)_6\ Mo_7O_{24}\ .\ 4\ H_2O$ in 400 ml distilled water and adjust the pH to 7-8 with the silica-free reagent 50% NaOH. Dilute to 500 ml and store in a polyethylene bottle.
Oxalic acid solution:	Dissolve 10 gm $(COOH)_2\ .\ 2H_2O$ in distilled water. Dilute to 100 ml and store in polyethylene bottles.

Reducing solution: Dissolve 1 gm 1-amino-2-naphthol-4-sulphonic acid and 2 gm anhydrous sodium sulphite in 100 ml distilled water. Add this solution to a solution of 60 gm sodium bisulphite dissolved in 300 ml of distilled water. This solution will keep several weeks if stored in a polyethylene bottle in a refrigerator.

Standard silica stock solution: Dissolve 4.73 gm sodium metasilicate monohydrate ($Na_2SiO_3 \cdot 9H_2O$) in freshly boiled and cooled distilled water and dilute to about 900 ml. Analyze a 100 ml aliquot gravimetrically and adjust the remainder of the solution to contain exactly 1.0 gm SiO_2 per litre. Store in a tightly stoppered polyethylene bottle.

Standard silica working solution, 1 ml = 0.02 mg SiO_2: Dilute 20 ml of the standard stock solution to 1000 ml with recently boiled and cooled distilled water. Store this solution in a polyethylene bottle.

Preparation of Calibration graph

Measure 0 (i.e. a blank), 1, 2, 4, 5, 10, 15, and 20 ml aliquots of the standard silica working solution into 100-ml plastic dishes. Add 10 ml dilute hydrofluoric acid (1:2000) and let stand 15-30 minutes. Place 10 ml borate buffer solution in 100-ml Nessler tubes. Transfer each sample from its dish to a tube and dilute to 100 ml.

Add in rapid succession 2.0 ml dilute hydrochloric acid and 4.0 ml ammonium molybdate solution. Stopper the tube with a rubber stopper and mix by inverting. Let stand 5-10 minutes. Add 3.0 ml oxalic acid solution and mix thoroughly. Measuring time from the addition of oxalic acid, wait for at least 2 minutes, but not more than 15 minutes, then add 4.0 ml reducing solution and mix thoroughly. After 10 minutes, read standards and blank against distilled water at 815 mμ using 1-cm and 5-cm cells and the red-sensitive photocell. Prepare a calibration curve by plotting mg SiO_2 in 113 ml as abscissae against optical density as ordinate for both path-length cells.

PROCEDURE

A. Preliminary Treatment

1. *Solid Samples*

Weigh 1.0 gm into a 100-ml beaker. Carry through a reagent blank. Add 5 ml hydrochloric acid, cover with a watch glass and warm to dissolve. Filter off any residue on a 7-cm Whatman No. 40 paper. Transfer the paper and residue to a 25-ml platinum crucible and ignite over a burner. Add silica-free sodium carbonate equivalent to six times the residue obtained. Fuse over a burner until a clear melt is obtained. Transfer the cooled melt to a 250-ml beaker, and cautiously add the filtrate previously obtained, taking care to avoid loss by ebullition. When the reaction is complete, add additional hydrochloric acid if necessary to assure complete neutralization of the carbonate. Transfer the solution quantitatively to a 250-ml volumetric flask and make to the mark.

2. *Solution Samples*

Take a suitable aliquot, or make a preliminary dilution if necessary and take an aliquot of this.

B. Colour Development

Transfer aliquots of the sample solutions estimated to contain 0.2 mg SiO_2 to 150-ml platinum dishes, or 250-ml polyethylene beakers. Carry through a

blank determination. Add 10 ml of dilute hydrofluoric acid solution to each and let stand 15 to 30 minutes. Place 10-ml portions of borate buffer solution in 100-ml Nessler tubes. Transfer each sample from its dish to a Nessler tube, quickly dilute to 100 ml and mix.

Add in rapid succession 2.0 ml dilute hydrochloric and 4.0 ml ammonium molybdate solution. Stopper the tube with a rubber stopper and mix by inverting. Let the solutions stand for 5-10 minutes. Add 3.0 ml oxalic acid solution and mix thoroughly. Measuring time from the addition of oxalic acid, wait for at least 2 minutes, but not more than 15 minutes then add 4.0 ml reducing solution and mix thoroughly. Wait 10 minutes, then read the sample against the blank in 1-cm cells at 815 mμ using the red-sensitive photocell. Record the optical density and read the mg SiO_2 per 113 ml from the previously prepared calibration graph. Record this value.

CALCULATIONS

$$\% \ SiO_2 = \frac{\text{mg } SiO_2 \text{ (graph)}}{1000 \times \text{sample wt, gm.}} \times \frac{\text{final dilution}}{\text{aliquot taken}} \times 100$$

$$\text{gm/l } SiO_2 = \frac{\text{mg } SiO_2 \text{ (graph)}}{1000 \times \text{sample vol.}} \times \frac{\text{final dilution}}{\text{aliquot taken}} \times 1000$$

If no colour is obtained, report the result as "less than" the minimum amount detectable, an actual figure based on the sample taken and dilutions used. The minimum amount detectable is 0.02 mg SiO_2 and the value to report can be calculated on this basis.

$$\text{gm/l } SiO_2 = \text{less than } \frac{0.02}{1000 \times \text{sample vol.}} \times \frac{\text{final vol.}}{\text{aliquot taken}} \times 1000$$

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The Iodometric Determination of Polythionates in Leach Liquors using Sodium Hydroxide

METHOD S_nO_6-1

SCOPE

This method is intended for the rapid determination of polythionates in acid leach liquors. The groups determined are S_nO_6'' when n = 4, 5, and 6. Results are reported as $Na_2S_4O_6$.

RANGE

The method is suitable for the determination of polythionates in the range 0.01 gram per litre (as $Na_2S_4O_6$) and up.

OUTLINE

Sodium hydroxide reacts with polythionates according to the following equations: (1)

(1) $S_6O_6'' \longrightarrow S_5O_6'' + S$

(2) $2\ S_5O_6'' + 6\ OH' \longrightarrow 5\ S_2O_3'' + 3\ H_2O$

(3) $4\ S_4O_6 + 6\ OH' \longrightarrow 5\ S_2O_3'' + 2\ S_3O_6'' + 3\ H_2O$

The S_3O_6'' ion is stable in dilute alkaline solution and is therefore not determined by this method. The S_2O_3'' is then titrated by iodine in the usual way

$$2\ S_2O_3'' + I_2 \longrightarrow 2I' + S_4O_6''$$

using chloroform as an indicator since starch is not effective at the low iodine concentration employed (2). The metal ions in the solution precipitate when the sodium hydroxide is added and are removed by centrifuging before titrating. While hexa-, penta- and tetrathionate are all included in the titration obtained, the result is calculated in terms of sodium tetrathionate according to equation 3.

The volumetric factor employed is given by,

$$\text{grams per litre } Na_2S_4O_6 = \frac{4}{5} \times 270 \times N \times \frac{T}{1000}$$

where N is the normality of the iodine solution used and T is the volume of the titration in ml.

Formaldehyde solution is added to the sample to inactivate any sulphite which might be present in the solution and prevent it being titrated by the iodine solution (3).

APPARATUS

Centrifuge:	Similar to International Size 1 Type C with 4 place 250 ml head.
Centrifuge bottles:	250 ml size.
Filter paper:	Whatman No. 30, 11 cm size.
Erlenmeyer flasks, with ground glass stopper:	250 ml size.
Pipette, volumetric:	50 ml size.
Burette:	10 ml micro burette.

REAGENTS

0.5N NaOH:	20 grams reagent grade NaOH per litre.
0.1N H_2SO_4:	Approx. 3 ml concentrated H_2SO_4 per litre.
Formaldehyde solution:	40% formaldehyde solution, reagent grade.
Iodine solution 0.004N:	Dissolve 0.508 grams of resublimed iodine in a saturated solution of 0.7 grams KI, and dilute to 1 litre—or dilute 10 ml of 0.1N iodine solution to 250 ml.
Chloroform indicator:	Reagent grade chloroform.

PROCEDURE

Pipette a 50-ml sample of leach liquor into a 250-ml centrifuge bottle. Add 50 ml of 0.5N NaOH, and centrifuge. Decant the supernatant liquid through a Whatman No. 30 filter paper, collecting the filtrate in a 250-ml Erlenmeyer flask with a ground glass neck. Wash the precipitate in the centrifuge bottle by repulping three or four times with 20-ml portions of water, centrifuging and decanting through the same paper.

Neutralize the filtrate to litmus with 0.1N H_2SO_4. Add 5 ml 40% formaldehyde and 2 ml of chloroform as indicator. Titrate with standard 0.004N iodine solution, stoppering and shaking vigorously after each addition as the end-point is approached.

The end-point has been reached when a red-violet colour, which does not disappear on shaking, appears in the chloroform layer. Carry out a blank titration, with 100 ml water and 2 ml of chloroform. Subtract the amount of iodine solution required to produce the same coloration in the chloroform layer of the blank, from the titration obtained with the sample.

CALCULATIONS

$$\text{grams } Na_2S_4O_6 \text{ per litre} = \frac{4}{5} \times 270 \times N \times \frac{T}{V}$$

where N = normality of iodine solution

T = iodine titration, ml. (corrected for blank)

V = sample volume, ml.

If the titration obtained is less than 0.5 ml of 0.004N iodine solution, the amount of polythionates shall be reported as less than the minimum amount detectable, (an actual figure based on sample volume used) rather than using the term "not detected". The figure to report for a 50-ml volume would be:

$$\frac{4}{5} \times 270 \times 0.004 \times \frac{0.5}{50} = < 0.01 \text{ gram } Na_2S_4O_6 \text{ per litre}$$

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The Determination of Total Solids, Total Ignited Solids, and Undissolved Solids (Suspended Slimes) in Mill Solutions

METHOD SOL-1

SCOPE

This method is intended to provide a standardized procedure for carrying out the various "solids" determinations, both as an aid to comparing results, and as a means for preparing such materials for spectrographic analysis.

RANGE

The range for these determinations depends entirely on the amount of sample available. A lower limit of 0.1 gm/l is possible using a 100-ml sample. This is inadequate for undissolved solids determination in which case 2 litres of sample are required, giving a limit of 0.005 gm/l (5 ppm).

OUTLINE

Total solids are determined by evaporating a known volume of solution to dryness on the steam bath, finishing in an oven at 110° C.

Total ignited solids are determined by igniting the total solids over a Meker burner to remove sulphuric acid and organic matter, and to convert most of the metallic salts to oxides.

Undissolved solids (suspended slimes) are determined by filtering a sufficiently large volume through a tared Gooch crucible, washing, drying at 110° C, and weighing.

APPARATUS

Beakers, Pyrex, Griffin low-form:	150 ml size.
Crucibles, Gooch:	Coors porcelain No. 4.
Crucible holders, Sargent:	
Flasks, filtering:	2000 ml size.
Rubber stoppers:	Size No. 9.
Funnels, Bunsen filtering, plain:	65 mm. size.

REAGENTS

Asbestos suspension:	Digest long-fibered asbestos with concentrated hydrochloric acid on the steam bath for 1 hour. Filter on a Buchner funnel and wash free of chloride. Suspend in water to form a free-running slurry, decanting off slimes and separating out hard lumps so only fibres remain.

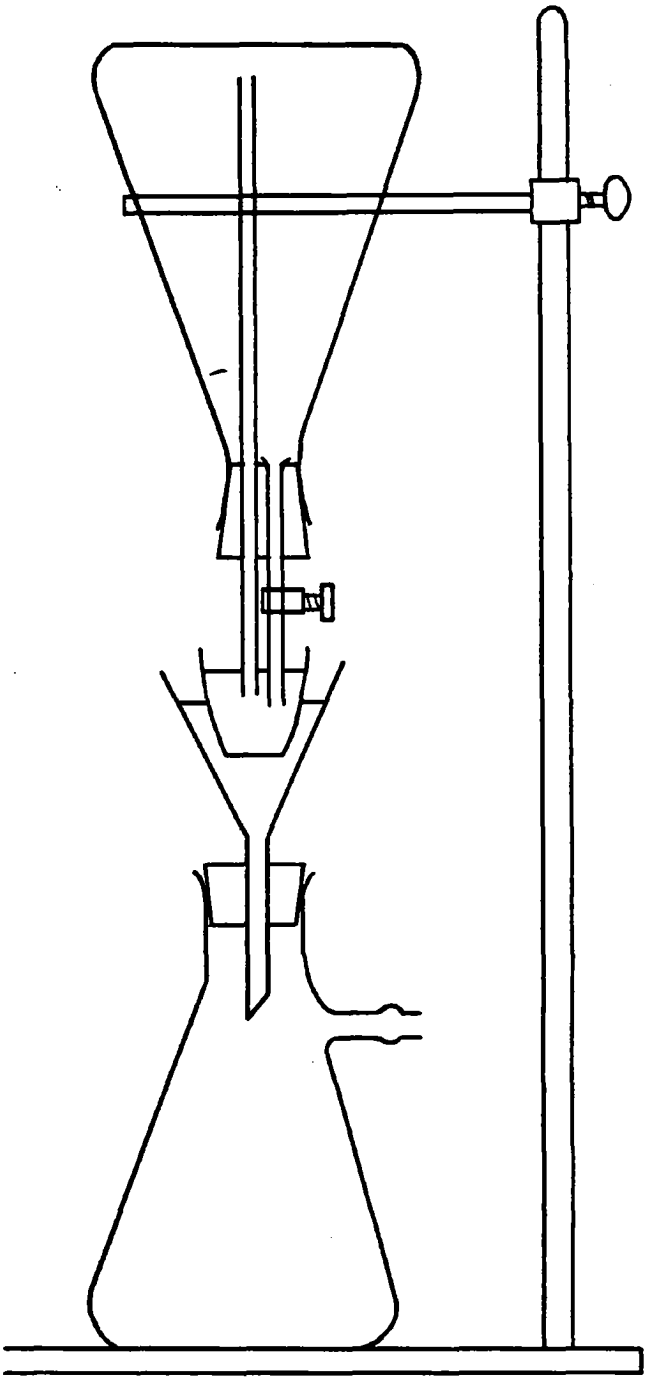

Figure 1
AUTOMATIC FILTRATION APPARATUS

Sulphuric acid solution, ¼%: 1.25 ml of 1:1 v/v sulphuric acid in 500 ml of water.

Sodium carbonate solution, ¼%: 1.25 gm of sodium carbonate in 500 ml of water.

PROCEDURE

A. *Total Solids*

Pipette 100 ml of sample into a tared 150-ml beaker. Evaporate to dryness on the steam bath. Carefully rinse off the outside of the beaker with distilled water, wipe, and dry in the oven at 110°C. Cool in a desiccator and weigh. Repeat the oven-drying to constant weight. If the sample is visibly wet with sulphuric acid, carry on with the ignition procedure below. Otherwise calculate the weight obtained to grams per litre total solids. If a spectrographic analysis of the solution was requested, transfer the dried residue *completely* to a glass or mullite mortar, powder thoroughly and bottle in a screw-cap shell vial. Submit to the spectrographic laboratory for semi-quantitative analysis, specifying any elements of particular interest. If major constituents only are desired, this should be stated on the label used.

Using the total solids figure, calculate the results of the spectrographic analysis to grams per litre.

B. *Total Ignited Solids*

If requested, or if the residue from A is visibly wet with sulphuric acid, fume over a gas burner till all trace of acid is removed. Cool in a desiccator and weigh. Repeat the ignition until constant weight is attained. Calculate the final weight to grams per litre total ignited solids. If a spectrographic analysis of the solution was requested, proceed as in A above.

C. *Undissolved Solids* (*Suspended Slimes*)

First prepare a Gooch crucible for filtration in the following manner. Insert a funnel in a rubber stopper and place in a 2000-ml filtering flask. Put a Sargent holder in the funnel and insert the crucible. Turn on the aspirator to apply vacuum to the flask. Stir up the asbestos suspension and pour enough in the crucible to give a pad 1-2 mm thick. Remove the crucible, tap gently to remove the pad, and reverse it in the crucible. Deposit a second fine layer on top of the first. Dry the crucible in an oven at 110°C. (Ignite to constant weight if the final residue is to be so ignited.) Cool in a desiccator and weigh.

Place the weighed crucible in the holder again. Shake the sample thoroughly. Measure a suitable volume (2 litres is suggested) into a beaker and filter through the crucible. An automatic device such as that shown in Figure 1 may be used if filtering is at all slow. In this case, transfer the measured volume directly to the Erlenmeyer flask, stopper, close the clamp and insert. Then slowly open the clamp and let the crucible fill up.

When all the solution has passed through the filter, note if the filtrate is sparkling-clear. If not, re-filter; or prepare a new Gooch pad and repeat on a fresh sample. Rinse the beaker or flask with three 50-ml portions of ¼% sulphuric acid for acid leach liquors or ¼% sodium carbonate for carbonate leach liquors, making sure to police all traces of insoluble matter that may have settled out in the vessel, into the crucible. Finally wash free of acid or carbonate with distilled

water. Dry at 110°C to constant weight. Cool in a desiccator and weigh (or ignite over a Meker burner, if specified). The increase in weight of the crucible is calculated as grams per litre undissolved solids or grams per litre undissolved solids (ignited), as required.

CALCULATIONS

A. and B.

$$\text{grams per litre total solids} = \frac{\text{wt of residue}}{\text{sample vol. ml}} \times 1000$$

C.

$$\text{grams per litre undissolved solids} = \frac{\text{wt of residue}}{\text{sample vol. ml}} \times 1000$$

The Preparation of a Tantalum-Niobium Concentrate and the Spectrographic Determination of the Tantalum-Niobium Ratio

METHOD Ta-1

SCOPE

This method is intended for the determination of tantalum in all types of material.

RANGE

The range is limited by the necessity to obtain sufficient material for the subsequent spectrographic determination. Furthermore, for accuracy, the spectrographic analysis must at least be carried through in triplicate. The lower limit, therefore, based on a 10-gram sample, would be about 0.05%.

OUTLINE

There does not exist, at the present time, a sensitive chemical method for tantalum. The method described here yields a concentrate containing all the tantalum and niobium in the sample, which is then examined spectrographically to determine the tantalum-niobium ratio. Since the niobium content can be determined rapidly and accurately by the thiocyanate colorimetric method, Nb-1, the tantalum content can be calculated from these two figures.

Silica is removed by treatment with hydrofluoric acid. The oxides of the earth acids are then taken up in concentrated hydrochloric acid with the aid of hydrogen peroxide. Subsequent dilution and boiling with sulphurous acid results in hydrolysis and quantitative precipitation of niobium and tantalum (1, 2). Tungsten and molybdenum are also precipitated, along with smaller amounts of titanium and vanadium.

In many cases, it is necessary to carry out only one hydrolytic precipitation. If a high degree of accuracy is required, a double hydrolytic precipitation should be used, however.

Complete hydrolysis of niobium and tantalum is sometimes difficult to obtain and this is particularly true if much titanium is present.

The hydrolytic precipitate is weighed and mixed with twice its weight of lithium carbonate as a spectrographic buffer.

A portion of the mixture is then transferred to a graphite electrode and this electrode as anode is excited in a D.C. type arc. The intensity ratio of the 3311.0 tantalum line to the 3310.5 niobium line is determined by densitometry and the corresponding weight ratio of tantalum to niobium is read off a previously prepared calibration graph (2).

APPARATUS

Dishes, platinum, flat bottom:	50 ml size.
Beakers, Griffin low form:	600 ml size.
Funnels, filtering, Bunsen, long stem, fluted:	65 mm dia.
Filter paper:	Whatman No. 40 or No. 541.
Funnel support:	
Furnace, muffle:	
Vials, screw cap:	4 ml size.
Hot plate:	
Spectrograph:	capable of resolving the 3310.5Nb line from the 3311.0 tantalum line.
D.C. arc source, or multi-source unit:	
Film, or plates:	Eastman Spectrum Analysis No. 2.
Densitometer:	
Electrodes:	anode—centre-post crater-type graphite electrode cathode—plain graphite.
Film processing equipment:	
Mortar and pestle:	glass, and alundum or agate.

REAGENTS

Hydrochloric acid:	
Hydrofluoric acid:	
Nitric acid, dil:	1/1, v/v.
Sulphuric acid, dil:	1/1, v/v.
Hydrochloric acid, 1%:	10 ml concentrated hydrochloric acid diluted to 1 litre.
Hydrogen peroxide, 30%:	
Ammonium hydroxide:	
Sulphur dioxide, saturated solution:	
Standard tantalum solution:	Fuse 100 mg tantalum pentoxide (Ta_2O_5) with 4 grams of finely ground sodium pyrosulphate in a 30 ml silica or quartz crucible. Cool, dissolve the melt in 1M tartaric acid and dilute to the mark in a 500 ml volumetric flask with 1M tartaric acid. 1 ml = 0.2 mg Nb_2O_5.
Standard niobium solution:	Fuse 100 mg of niobium pentoxide (Nb_2O_5) with 4 gm finely ground sodium pyrosulphate in a 30 ml silica or quartz crucible. When cool, dissolve the melt in 1M tartaric acid and dilute to the mark in a 500 ml volumetric flask with 1M tartaric acid. 1 ml = 0.2 mg Nb_2O_5.
Lithium carbonate:	

PROCEDURE

A. *Preliminary Preparation*

Weigh out a suitable portion of the sample (up to 10 gm) into a platinum dish. If the sample has been shown, by the previously carried out niobium analysis, to contain no niobium, pipette an aliquot of the standard niobium solution containing an amount of niobium equivalent to the estimated tantalum content, onto the sample and evaporate to dryness.

Add 10 ml of 1:1 nitric acid and 2 ml of 40% hydrofluoric acid and again take the sample slowly to dryness. Repeat this procedure until the ore appears to be decomposed. Cool. Add 20 ml 1:1 sulphuric acid and take the sample to dense fumes. Cool. Wash down the sides of the platinum dish with distilled water and fume the sample again. Repeat this part of the procedure, finally taking the solution to dryness.

Add 5 ml of concentrated hydrochloric acid to the dish and warm the sample. Wash the contents of the dish into a 600-ml beaker with about 50 ml distilled water, using a rubber policeman if necessary. Add 20 ml of concentrated hydrochloric acid and 15 ml of 30% hydrogen peroxide to the beaker. Warm the covered solution gently for 5-10 minutes to assist the solution of earth acids and titania. Dilute the solution to 300 ml and boil for 30 minutes. Cool. Filter the precipitate on Whatman No. 541 or No. 40 filter paper, wash with 1% hydrochloric acid solution and reserve the precipitate for further treatment. Evaporate the filtrate to about 250 ml, neutralize with ammonium hydroxide and add 5 ml of concentrated hydrochloric solution. Add 25 ml of a saturated solution of sulphur dioxide and adjust the sample volume to about 300 ml. Boil for about 20 minutes and allow the precipitate to settle for at least 4 hours. Filter the precipitate on Whatman No. 541 or No. 40 filter paper, wash with 1% hydrochloric acid and combine the two hydrolytic precipitates. Ignite the precipitates at 800°-900° C.

Weigh the ignited precipitate and transfer to a glass or alundum mortar. Add a weight of lithium carbonate equal to twice the weight of the precipitate. Thoroughly grind and mix, and transfer to a 4-ml screw-cap vial for transmission to the spectrographic laboratory.

B. *Spectrographic Finish*

Transfer a portion of the lithium carbonate : earth acid mixture to the crater of a centre-post crater-type graphite electrode. Insert in the lower (anode) electrode clamp using a plain graphite counter-electrode (cathode) as the upper electrode. Space the electrodes 2 mm apart. Excite the electrodes by means of a D.C. arc or an A.R.L. multi-source unit with the following settings: capacitance 60 mf, inductance 400 microhenries, resistance 20 ohms. Pre-arc for 30 seconds, then open the shutter for 10 seconds. Record the spectrum on Eastman Spectrum Analysis No. 2 plates, and process. Densitometer the 3311.0 tantalum line and the 3310.5 niobium line and report their ratio. Determine the weight ratio of tantalum to niobium from a previously prepared graph, in which intensity ratio Ta 3311.0/Nb 3310.5 is plotted as ordinate against weight ratio of tantalum to niobium.

CALCULATION

$$\% \, Ta_2O_5 = \% \, Nb_2O_5 \times \text{wt. ratio} \, \frac{Ta_2O_5}{Nb_2O_5}$$

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The Colorimetric Determination of Titanium with Ascorbic Acid

METHOD Ti-1

SCOPE

The method is intended for the determination of titanium in the lower ranges. It is less subject to interference from other ions than the peroxide method.

RANGE

The lower limit of the method as outlined here is 0.005%, based on a 2-gram sample. This may be further reduced by developing the colour in a 25-ml volume, and by using longer cells in the spectrophotometer.

OUTLINE

Ascorbic acid, like many other reagents containing one ene-diol group (—COH:COH—), reacts with titanium to give a yellow coloured product. The colour has maximum absorbancy over a wave length range of 330 to 400 mμ and is approximately three times as intense as the titanium-peroxide colour (1). Attainment of maximum colour intensity is dependent upon the concentration of reactants, the order in which they are added, and the pH of the solution. There is no fading in 12 hours and no Beer's law deviation below a concentration of 2 mg in the 50 ml final volume.

The influence of ascorbic acid concentration on colour intensity is reduced to a minimum by maintaining an ascorbic acid/TiO_2 mole ratio of more than 50 to 1. The pH of the titanium solution to which the ascorbic acid is added should be less than 1.5, and the final pH must be between 3.5 and 6.0.

Fluoride interferes seriously, by forming the very stable titanium fluoride complex. Phosphate, molybdate, vanadate and silicate all interfere if more than 5 mg is present in the final aliquot taken for colour development.

The following ions, at concentration corresponding to 50 mg in the final solution, are stated not to interfere: aluminum, barium, calcium, cobaltous, chromic, cupric, ferrous, ferric, potassium, magnesium, manganous, sodium, ammonium, nickelous, strontium, tungstate, chloride, nitrate and sulphate (2).

Silica is removed during the preliminary fuming with hydrofluoric acid, and any fluoride originally present is volatilized, along with the added HF, in the subsequent fuming with perchloric acid. To insure complete expulsion of the fluoride, the solution should be diluted, the sides of the dish washed down and the solution fumed again. This treatment must be repeated several times. It must be emphasized that fuming should not be continued to anywhere near complete expulsion of the perchloric acid. Not only are the deposited salts hard to re-dissolve if this occurs, but there is even possibility of volatilization of the

titanium as fluoride. Titanium hydrolyzes readily in solutions of low acidity, and titanium phosphate, which is insoluble even in very acid solutions, will separate if titanium and phosphate are both present in sample solutions (3).

Titanium is separated from molybdenum, vanadium, phosphorus, chromium and uranium, using a sodium carbonate-sodium peroxide separation. Iron is added as a carrier for this separation since unless at least ten times as much iron as titanium is present, losses are likely to occur. The peroxide solution must be boiled at least 10 minutes to break up the complex titanium-peroxide ion, which, as first formed, is very soluble.

In re-dissolving the precipitate after the sodium peroxide separation it is preferable to use a hot solution of 10% ammonium sulphate in 1:1 sulphuric acid, since the titanium compound is more soluble in this mixture.

APPARATUS

Beakers, Griffin low form, Pyrex:	100, 250 and 400 ml sizes.
Funnels, 60°, fluted Pyrex:	
Filter paper Whatman No. 50:	11 cm.
Hot plate:	
Steam bath:	
Dishes, platinum:	50 ml size.
Pipettes:	10, 20, 25 ml sizes.
Burette, micro:	10 ml size.
Flasks, volumetric:	50, 100, 250, 500 ml sizes.
pH meter, glass electrode:	Beckman Model H-2.
Spectrophotometer, Beckman Model B:	
Spectrophotometer cells, Corex:	1 cm light path.
Spectrophotometer cells, Corex:	5 cm light path.

REAGENTS

Nitric acid, concentrated:	
Hydrochloric acid, concentrated:	
Sulphuric acid, concentrated:	
Perchloric acid, concentrated:	
Hydrofluoric acid, 48%:	
Acetic acid, glacial:	
Sulphuric acid, 1:1:	v/v.
Sulphuric acid, 10%:	v/v.
Sulphuric acid, 5%:	v/v.
Ammonium sulphate in dilute sulphuric acid solution:	Dissolve 50 gm ammonium sulphate in 500 ml 1:1 sulphuric acid solution.

Sodium carbonate:	
Sodium peroxide, 10%:	w/v, prepared fresh.
Sodium peroxide, 5%:	w/v, prepared fresh.
Sodium hydroxide, 10%:	Prepared by diluting reagent 50% solution (e.g. B and A Code 2327). Prepare and store in polyethylene bottles.
Ascorbic acid reagent:	Dissolve 1 gm sodium bisulphite in 50 ml distilled water and add 2.5 gm of l-ascorbic acid. Make to 100 ml with water.
Standard titanium solution:	Dissolve 0.0100 gm of TiO_2 in 10 ml concentrated sulphuric acid containing 0.1 gm ammonium sulphate and *cautiously* dilute to about 75 ml with water. Transfer to a 100 ml volumetric flask and make to the mark. 1 ml of this solution contain 100γ TiO_2.

Preparation of the Calibration Curve

By means of a 10-ml microburette, transfer 0, 1, 2, 4, 6, 8 and 10-ml portions of the standard solution to a series of 100-ml beakers and dilute to 20 ml volume with 1% sulphuric acid. Adjust the acidity to give a pH in the range 1.0 to 1.5 (using a pH meter). Add 10 ml of ascorbic acid reagent solution and 5 ml of glacial acetic acid, and mix well. Adjust the pH to 5.0, using 10% sodium hydroxide solution, and transfer to 50-ml volumetric flasks. Dilute to the mark and mix. Measure the absorbancy of the solutions in 1-cm cells against the reagent blank, using the Beckman Model B spectrophotometer at a wave length of 360 mμ. In addition, measure the absorbancy of the first three standards in 5-cm cells. Plot curves of mg TiO_2 per 50 ml volume as abscissa versus absorbance as ordinate for both cell path-lengths.

PROCEDURE

A. Sample Preparation

1. *Solid Samples*

Weigh a suitable amount of sample (Table 1) into a 50-ml platinum dish. Add 5 to 10 ml nitric acid cautiously, and when any initial reaction has subsided, digest on a padded portion of the hot plate for 10 minutes. Remove, cool, and add 5 ml each of perchloric acid and hydrofluoric acid. Replace on the hot plate and take to fumes, but do not fume dry. Repeat the addition of hydrofluoric acid, replacing any perchloric acid that has been fumed off each time, until all the silica has been removed. Then bring the perchloric acid volume to about 10 ml and fume down to about 5 ml to remove the bulk of the fluoride. Cool the solution and transfer the contents of the platinum dish completely to a 250-ml beaker, using a minimum of 10% sulphuric acid (about 50 ml in all). Take to dense fumes. Cool, rinse down the sides and fume again, making sure the beaker does not go dry by adding sulphuric acid as needed. Cool, dilute to 50 ml, and add 10 ml of 5% ferric sulphate solution. Neutralize by adding sodium carbonate in small amounts with vigorous stirring. Transfer the contents of the beaker completely to a 400-ml beaker containing 50 ml of cool 10% sodium peroxide solution. Set on the steam bath and digest at 75° C. for not less than 30 minutes. Filter through a No. 50 Whatman filter paper and wash with a minimum of 5% sodium peroxide solution.

Dissolve the precipitate using hot concentrated HCl, followed by a wash with hot 10% ammonium sulphate in dilute sulphuric acid. Transfer the paper,

including any insoluble material, to a platinum dish. Dry, ignite and fuse any residue with a small amount of sodium carbonate. Dissolve in a minimum of hydrochloric acid and combine with the main solution. Alternatively treat with nitric, perchloric and hydrofluoric acids as described in the first part of the procedure.

Transfer the complete solution to a volumetric flask of the proper size (Table 1) and dilute to the mark with 5% sulphuric acid.

2. *Solution Samples*

Pipette a suitable aliquot into a 50-ml platinum dish, evaporate on a steam bath to dryness, and proceed as for solid samples.

B. Colour Development

NOTE: Prepare a blank employing the reagents used in colour development.

Pipette the proper aliquot (Table 1) into a 100-ml beaker and adjust with 10% sodium hydroxide until the acidity as measured by a pH meter, is in the pH range 1.0 to 1.5. Add 10 ml of ascorbic acid solution followed by 5 ml of glacial acetic acid and stir. Adjust the pH to 5.0 with 10% sodium hydroxide, transfer to a 50-ml volumetric flask and make to the mark with water. Mix well and read the absorbance on the Beckman Model B spectrophotometer in 1-cm cells (or 5-cm cells if required) at a wave length setting of 360 mμ, against a reagent blank.

Determine the mg of TiO_2 per 50 ml volume using the previously prepared calibration graph.

Table 1

Dilution Table for Titanium Determination

Solid Samples

Range, %	Take gm	Dilute to final volume ml	Take Aliquot ml
below 0.005	2	(use 5-cm cells)	
0.005 to 0.05	2	do not dilute	
0.05 to 0.20	2	100	25
0.20 to 1.0	1	250	20
1.0 to 5.0	1	500	10

Solution Samples

Range gm/l	Take ml	Dilute to final volume ml	Take Aliquot ml
below 0.005	20	(use 5-cm cells)	
0.005 to 0.05	20	do not dilute	
0.05 to 0.20	20	100	25
0.20 to 1.0	10	250	20
1.0 to 5.0	10	500	10

CALCULATIONS

$$\% \text{ TiO}_2 = \frac{\text{mg TiO}_2 \text{ in 50 ml}}{1000} \times \frac{\text{final volume}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

$$\text{gm/l TiO}_2 = \frac{\text{mg TiO}_2 \text{ in 50 ml}}{1000} \times \frac{\text{final volume}}{\text{aliquot taken}} \times \frac{1000}{\text{sample vol.}}$$

If the sample gives approximately the same reading as the blank, the amount of TiO_2 should be reported as less than the minimum amount detectable, (an actual figure based on the sample weights and volumes used). The minimum amount detectable may be considered as 0.1 mg in 1-cm cells, and 0.02 mg in 5-cm cells and the figure to report if 5-cm cells were used may be calculated on this basis, i.e.

$$\% \text{ TiO}_2 = \text{less than } \frac{0.02}{1000} \times \frac{\text{final volume}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

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The Peroxide Colorimetric Determination of Vanadium in Uranium Concentrates

METHOD V-1

SCOPE

This method is intended primarily for use in the determination of vanadium in chemically-produced uranium concentrates.

RANGE

The method covers the range 0.25% and up, based on a 2-gm sample and 1-cm spectrophotometer cells.

The range can be extended by using larger samples and 5-cm cells.

OUTLINE

In acidic solutions, the pale yellow pervanadyl ion instantly forms the deep red-brown mono-peroxy-pervanadyl cation when hydrogen peroxide is added (1).

$$VO_2^+ + H_2O_2 \rightleftharpoons (VO(O.O))^+ + H_2O$$

Acidity can vary over a wide range (0.6 to 6N for sulphuric, nitric and hydrochloric acids) (2, 6), and the solution can contain 0.5 to 3 ml of 3% hydrogen peroxide per 100 ml, without affecting the colour development. Larger amounts of peroxide decrease the colour, but the extent of the diminution is reproducible (up to 10 ml 3% H_2O_2) (2). Perchloric acid may also be used as a medium for the determination (3) and has the effect of diminishing the overall colour due to uranium and iron, as compared to the sulphuric acid medium.

The vanadium-peroxide colour exhibits maximum absorption from about 450 to 490 mμ. The absorption band is very broad however, and the colour can be read effectively from 440 to 550 mμ. It obeys Beer's law (3).

Neither iron nor uranium interfere if the developed colour is read at 510 mμ. Iron shows no absorption above a wave length of 480 mμ in sulphuric acid solution, nor above 420 mμ in perchloric acid. With uranium, the corresponding wave lengths are 500 and 490 mμ (4, 5). Presence of peroxide does not affect the latter values at all. Fluoride, added to bleach the titanium colour, reduces the uranium colour, but only very slightly (5). Molybdenum, in quantities equivalent to vanadium, does not absorb above a wave length of 450 mμ (3). It has never been found in Canadian concentrates in large amounts. Titanium, which is more commonly found, interferes very seriously. The colour is about four times that of vanadium at 440 mμ and equal to it at 510 mμ (3). The interference can, however, be completely eliminated by the addition of fluoride which bleaches the titanium compound, but has no effect on the vanadium colour. Kleiner (6) reported that this was due to the formation of a colourless titanyl fluoride ion, but the evidence for this has recently been questioned (7), and it is postulated instead

that the bleaching is a solvent effect caused by a slight alteration in the crystal field bands, and due to a change in the point dipole moment for the second co-ordination sphere. The effect of chromium was studied by Foster (8), who found only a slight interference caused by an amount of this ion equal to the amount of vanadium present (although this work was carried out in the 425 mμ region). Tungsten is also stated to interfere (3). Neither of these elements occur commonly in the uranium concentrates. Large amounts of other coloured ions (nickel, cobalt) may interfere, but can be compensated for by reading against an equivalent amount of the sample in which the colour has not been developed. Ordinarily this is not necessary. Bromides and iodides would be expected to interfere, since hydrogen peroxide liberates yellow coloured bromine and iodine from them, but these are not likely to be present.

The low sensitivity of the method make it unsuitable for the determination of vanadium in ores and residue. For these, the phosphotungstovanadic acid method (METHOD V-2) is preferred.

Use of plastic spectrophotometer cells is sometimes recommended, but the experience here has been that liberation of bubbles of oxygen at the plastic surface makes it almost impossible to carry out the determination. Therefore an old set of Pyrex cells is set aside and blanks are run occasionally to check them.

APPARATUS

Beakers, Griffin low form:	150 ml, 250 ml sizes.
Funnels, filtering Bunsen long stem:	
Filter paper, Whatman No. 41 H:	
Flasks, volumetric:	100 ml size.
Pipettes:	50 ml size.
Spectrophotometer, Beckman Model B:	
Spectrophotometer cells, Pyrex, 1 cm and 5 cm:	Use sets that are unsuitable for other work and reserve for this determination.

REAGENTS

Nitric acid, 1:1:	v/v.
Perchloric acid, concentrated 70%:	
Hydrogen peroxide, 3%:	Dilute concentrated 30% hydrogen peroxide with 9 parts of water.
Hydrofluoric acid:	Dilute concentrated 48% hydrofluoric acid with 9 parts of water.
Standard vanadium solution:	Dissolve 2.3 gm ammonium metavanadate (equivalent to 1.000 gm V_2O_5) in 10 ml nitric acid and dilute to 1 litre. 1 ml = 1 mg V_2O_5.

Preparation of Colorimetric Calibration Graph

Carry a blank through the procedure. Pipette aliquots of the standard solution containing 2, 5, 10, 15, 20 mg V_2O_5 into 150-ml beakers. Add 10 ml concentrated perchloric acid and evaporate to fumes. Cool, dilute with water and transfer to 100-ml volumetric flasks. Add 5 ml of 3% hydrogen peroxide to each, dilute to volume and mix. Read the optical density of the standards

against the blank solution containing the same amount of acid, but no hydrogen peroxide, using 1-cm and 5-cm Pyrex cells, at a wave length of 510 mμ. Construct a calibration graph with optical density as abscissa and mg V_2O_5 per 100 ml volume as ordinates for both cell path-lengths.

PROCEDURE

Weigh a suitable sample containing 5 mg V_2O_5 or more (2 gm is suitable for concentrates near the specification limit). Add 10 ml dilute nitric acid (1:1, v/v). Warm to dissolve. Cool slightly, add 20 ml concentrated perchloric acid and heat to copious fumes. Cool again, add 50 ml water and warm to dissolve. Filter immediately through a Whatman No. 41H filter paper into a 100-ml volumetric flask, and wash the residue thoroughly with warm water. Cool the solution to room temperature, dilute to volume and mix well. Pipette 50 ml of the solution into a second 100-ml volumetric flask, leaving the remaining 50 ml in the first flask to serve as a blank. Add 5 ml of 3% hydrogen peroxide to the second flask only. Add 10 ml of dilute hydrofluoric acid to both solutions and dilute them to 100 ml with water. Mix well and measure the optical density of the developed peroxide colour against the undeveloped sample in a Beckman Model B spectrophotometer at 510 mμ in 1-cm Pyrex cells. Record the optical density and determine mg V_2O_5 per 100 ml from the calibration graph.

CALCULATIONS

$$\% \ V_2O_5 = \frac{\text{mg } V_2O_5 \text{ per 100 ml}}{1000} \times \frac{\text{final sol'n vol.}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt. gm}}$$

$$\text{gm/l } V_2O_5 = \frac{\text{mg } V_2O_5 \text{ per 100 ml}}{1000} \times \frac{\text{final sol'n vol.}}{\text{aliquot taken}} \times \frac{1000}{\text{sample vol. ml.}}$$

If no colour is obtained, report the V_2O_5 content of the sample as less than the minimum amount detectable. This may be taken as 2 mg per 100 ml volume and the figure to report calculated on this basis

$$\% \ V_2O_5 = \text{less than } \frac{2}{1000} \times \frac{\text{final sol'n vol.}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt. gm}}$$

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62314-0—33

Colorimetric Determination of Vanadium as Phosphotungstovanadic Acid Using Cupferron Extraction and Sodium Hydroxide Separation

METHOD V-2

SCOPE

The method outlined is intended for determining vanadium in ores containing elements such as titanium, molybdenum, chromium and niobium which interfere in the hydrogen peroxide colorimetric method (1). It may also be used on concentrates, precipitates and solutions, although the peroxide method will normally be used if these interferences are known to be absent.

RANGE

The colour of phosphotungstovanadic acid is very stable and moderately sensitive (2). Ores containing vanadium in excess of 0.01% can be determined, provided that the technique described is adhered to closely. In particular, the quantity of vanadium in the sample must be sufficient to ensure good yield in the separation.

OUTLINE

Quinquevalent vanadium gives with phosphoric acid and sodium tungstate in acid solution, a brownish colour which turns to yellow on standing or boiling. This colour is due to phosphotungstovanadic acid, a co-ordinated compound of the heteropoly type whose exact formula is obscure. Wright and Mellon (1) have shown that the optimum concentration of phosphoric acid is 0.5M, and of sodium tungstate, 0.025 M.

According to Sandell (2), potassium and ammonium ions interfere by forming slightly soluble heteropoly acids. Titanium, zirconium, bismuth, antimony and tin give slightly soluble phosphates or basic salts, except at low concentrations.

Molybdenum (VI) gives a yellow colour under the same conditions as vanadium, but only at relatively high concentrations (10 mg Mo is roughly equivalent to 0.14 mg V_2O_5) (3).

The interference of ferric iron in small amounts is claimed to be eliminated by the phosphoric acid present. In larger amounts (up to 0.1 gm Fe in the final aliquot) it produces a brownish hue which is considerably reduced in intensity by boiling. According to Cooper and Winter (3), 10 mg Fe is equivalent to 0.005 mg V_2O_5, although a more recent study found no interference from iron (4).

62314-0—33½

Chromate, copper, cobalt, nickel and other coloured ions interfere by their own colour. Chromium is the most important of these interfering ions, 10 mg being equivalent to 0.06 mg V_2O_5.

Tungstate ion exhibits some absorption at the wave length used, so that a reagent blank must be used as a reference solution.

The following ions do not interfere if present at less than 0.5 gm per 100 ml:— Mg, Ca, Sr, Ba, Zn, Cd, Hg^{II}, Al, Pb and As^{V}. SiO_2 below 0.05 gm as Na_2SiO_3, thorium below 0.01 gm and silver below 0.1 gm do not interfere (3).

Quinquevalent vanadium is separated from uranium, chromium, titanium, aluminum, arsenic and phosphorus by ether extraction of its cupferrate from 1:9 v/v sulphuric acid solution (5) (6). Sodium hydroxide precipitation is then used to separate soluble sodium vanadate from iron, titanium and zirconium, iron (about ten times the expected titanium content) being added to co-precipitate the titanium (7).

The phosphotungstovanadate colour is developed in the acidified filtrate and is read in 1-cm cells at 410 mμ, a wave length which gives maximum absorptivity when the solutions are read against the reagent blank.

The colour is slightly temperature sensitive. This may be compensated for in careful work by carrying standards through the procedure and ensuring that standards and samples are at the same temperature when read.

APPARATUS

Beakers, Griffin, low form:	250 ml, 400 ml.
Separatory funnels, Squibb pear shaped:	300 ml.
Funnel, Pyrex, 60°:	
Spectrophotometer, Beckman Model B:	
Spectrophotometer cells, Corex, 1 cm:	
Cooling bath:	Capable of giving 5°C. A bath 14″ × 28″ × 12″ deep will provide space for 10 separatory funnels and for the ether and cupferron solutions.

REAGENTS

Cupferron, 6% aqueous solution:	Store in a cold place.
Sodium tungstate solution:	16.5 grams sodium tungstate in 100 ml water.
Phosphoric acid solution:	50 ml of 85% phosphoric acid diluted to 100 ml with water.
Ethyl ether:	Freshly distilled peroxide-free.
Hydrofluoric acid solution, dilute:	10 ml of hydrofluoric acid 48% diluted to 100 ml with water.
Nitric acid solution:	1:1 v/v.
Ferric chloride:	10 grams ferric chloride in 100 ml water containing a few drops of hydrochloric acid.
Sulphuric acid:	1:1, v/v.
Sodium hydroxide solution, 10%:	10 grams of sodium hydroxide in 100 ml water.
Potassium permanganate solution:	3 grams of potassium permanganate in 100 ml water.

Standard vanadium solution: Ignite vanadium pentoxide at 500°C for 1 hour. Dissolve 0.1000 gram of the ignited oxide in a slight excess of 10% sodium hydroxide solution. Cool, neutralize with dilute sulphuric acid (1:1) and add 10 ml in excess. Dilute to 1 litre. This solution contains 0.1 mg V_2O_5 per ml. It can be standardized if necessary by reducing the vanadium in a 100 ml aliquot with SO_2 in an acid solution, and titrating with standard 0.025N potassium permanganate solution.

Preparation of the Calibration Curve

Pipette aliquots of the standard solution containing from 0.1 to 4.0 mg V_2O_5 into 100-ml beakers. Add 2 ml of concentrated nitric acid and 2 ml of 1:1 phosphoric acid. Dilute to about 50 ml and boil for 2 minutes. Finally, add 5 ml of sodium tungstate solution, continue boiling for a few minutes, and cool. Transfer to a 100-ml volumetric flask and dilute to the mark. Read the optical density of the solution against a reagent blank in the Beckman Model B spectrophotometer at a wave length of 410 mμ (with no filter). Plot a graph with optical density as abscissa and milligrams of vanadium pentoxide per 100 ml volume as ordinate.

PROCEDURE

A. *Decomposition of the Sample*

Weigh 1 to 5 grams of the ore, depending on the vanadium content (Table 1) into a 250-ml beaker and add 10 ml concentrated nitric acid and 30 ml of concentrated hydrochloric acid. Transfer to a hot plate and boil gently until all traces of organic matter are destroyed. Add 10 ml of hydrofluoric acid, stir and evaporate almost to dryness. Add 10 ml of 1:1 sulphuric acid, 10 ml of perchloric acid and 10 ml of dilute hydrofluoric acid. Boil again and take to dense fumes. Cool, wash down the sides of the beaker and fume again until nearly dry. Dilute to 75 ml, boil for 15 minutes, filter on a No. 30 paper and wash the residue with hot water. Cool and add potassium permanganate solution until a faint pink colour persists. Cool the beaker to about 5°C.

B. *Cupferron Separation and Ether Extraction*

Transfer the cold solution to a 300-ml separatory funnel. Add cold 6% cupferron solution until no further precipitation takes place. Extract the cupferrates with three 50-ml portions of ethyl ether allowing 10 to 15 minutes for the phases to separate each time. Collect the ether extracts in a 250-ml beaker. Test the aqueous layer for completeness of the cupferron separation by adding a further portion of the cupferron solution. If the precipitate that forms is white, the separation is complete. Otherwise the extraction step must be repeated.

To the ether extract, add 10 ml of water, followed by 20 ml of 1:1 nitric acid. Cover with a ribbed watch glass and volatilize the ether on a hot water bath in the special hood provided for this purpose. When the ether is completely removed, transfer the beaker to a hot plate, add 5 ml each of 1:1 nitric acid and 1:1 sulphuric acid. Take just to fumes. Cool, add 5 ml each of 1:1 nitric acid and 1:1 perchloric acid. Take to dense fumes. Cool. Wash down the sides of the beaker and evaporate almost to dryness.

C. *Sodium Hydroxide Separation*

Take up the contents of the beaker in 50 ml of water and digest on the hot plate to dissolve. Adjust to pH 3-5 with 10% sodium hydroxide solution,

then add 2-3 ml of 10% ferric chloride solution. Stir, then add 20-30 ml of 10% sodium hydroxide solution in excess. Boil for at least 20 minutes, then set on a cooler part of the hot plate to digest for another 30 minutes at about 80°C. Filter on a Whatman No. 42 filter paper and wash with hot 1% sodium hydroxide solution.

D. *Colour Development*

(Prepare a reagent blank at the same time as the samples).

Neutralize the filtrate with nitric acid using methyl red indicator, and dilute as required depending on the vanadium content, (Table 1).

Table 1

Dilution Table

Range % V_2O_5	Take gm	Dilute to ml	Aliquot ml
0.005 – 0.02	5	do not dilute	
0.02 – 0.2	2	do not dilute	
0.2 – 2.0	1	250	50
2.0 – 10.0	1	250	10

Adjust the volume to 50 ml, evaporating if necessary, and bring to a boil. Add 2-3 ml of concentrated nitric acid and 2 ml of 1:1 phosphoric acid. Boil for about 2 minutes, add 5 ml of sodium tungstate solution and continue boiling for 2-3 minutes. Cool, transfer to a 100-ml volumetric flask and dilute to the mark. Measure the optical density of the solution, using a reagent blank to set the scale to zero, and reading at a wave length of 410 mμ (no filter) in 1-cm cells on the Beckman Model B spectrophotometer. If the solution remained coloured after the phosphoric acid addition and boiling, divide it and measure the optical density of an equivalent portion that has not had the tungstate reagent added, against a water blank. This can then be applied as a correction to the sample, read in the usual manner. The colouration is usually caused by uranium and iron in the final filtrate as a result of incomplete separation and it is, of course, preferable to repeat the determination if possible. The V_2O_5 content in mg per 100 ml is read off the calibration graph in the usual way.

CALCULATIONS

$$\% V_2O_5 = \frac{\text{mg } V_2O_5 \text{ per 100 ml}}{1000} \times \frac{\text{diluted volume}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

If the sample gives approximately the same reading as the blank, the amount of V_2O_5 should be reported as less than the minimum amount detectable (an actual figure based on the sample weights and volumes used), rather than using the term "not detected".

The minimum amount detectable may be taken as 0.2 mg V_2O_5 per 100 ml volume for readings in 1-cm cells and the value to report would be

$$\% V_2O_5 = \text{less than } \frac{0.2}{1000} \times \frac{\text{diluted vol.}}{\text{aliquot taken}} \times \frac{100}{\text{sample wt.}}$$

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The Gravimetric Determination of Zirconium (and Hafnium) in Ores, Mill Products and Solutions, Using Mandelic Acid

METHOD Zr-1

SCOPE

This method is intended for the determination of macro amounts of zirconium in ores, solutions and mill products. The method does not differentiate between hafnium and zirconium (3).

RANGE

From 10 to 300 mg of zirconium (plus hafnium) as the oxides, can be determined by this method with an accuracy of about 5 percent. Smaller amounts can be determined with a lesser degree of accuracy. For micro or semimicro amounts, a colorimetric finish is preferable.

OUTLINE

The determination of zirconium and hafnium with mandelic acid described here, is based primarily on the method described by C. A. Kumins (1). Zirconium mandelate is precipitated from a hydrochloric acid solution by adding an aqueous solution of mandelic acid and heating the solution at 85°C for 20 to 30 minutes. Interfering elements such as silica, phosphorus, fluorides and excess free sulphuric acid are removed prior to the mandelate precipitation by a sodium peroxide or sodium peroxide-sodium carbonate separation. This is accomplished by a water digestion of a sodium peroxide sinter or fusion of the sample or by adding an excess of caustic to the acid solution of the sample, followed by addition of hydrogen peroxide. A second sodium peroxide or sodium carbonate-sodium peroxide separation is advisable when large amounts of the above interfering elements are present. This separation also eliminates such elements as tungsten, chromium, tin, arsenic, lead and uranium. Double and even triple fusions of the impure zirconium mandelate precipitates with potassium carbonate are necessary to eliminate the interference of niobium and tantalum (2). Each fusion is water-leached, filtered and washed before re-fusing. Interference from complexing agents such as tartrates and citrates, in solution samples, is eliminated by evaporating an aliquot portion of the sample to dryness with sulphuric acid and either perchloric or nitric acid. In some cases it is advisable to do an ammonium hydroxide separation to remove excessive amounts of calcium, magnesium, nickel etc. This separation is usually done on an acid solution of the precipitate following the sodium peroxide or sodium peroxide-sodium carbonate separation.

APPARATUS

Analytical balance:	
Platinum crucibles:	30 to 40 ml capacity.
Funnels:	Bunsen filtering long stem Pyrex, fluted 65 to 75 mm dia.
Support, funnel:	6 hole.
Filter paper:	Whatman No. 42, 41H, 40, 30 in 12.5 cm, 11 cm and 9 cm sizes.
Peroxide bomb, electric ignition:	Parr series 2200, 42 ml cup. The assembly consists of one complete bomb with electric ignition head, fusion cup, bell body and screw cap coupling nut; *see* METHOD U-1.
Extra fusion cups:	Parr 115 AC.
Dust covers:	Parr 146 AC.
Wrench and bench socket:	
Water bath:	Parr Cat. No. A140 AC.
Peroxide dipper:	Parr Cat. No. A 34 CH.
Extra gaskets:	Parr Cat. No. 120 AC.
Ignition unit:	Parr Cat. No. 2901.
Crucible tongs:	Stainless steel.
Crucible tongs:	Platinum tipped.
Beakers:	600, 400, 250 and 150 ml Pyrex.
Watch glasses:	Pyrex smooth rim to fit above beakers.
Centrifuge:	Similar to International size 1 Model C50, with 4 place 250 ml head.
Centrifuge bottles:	250 ml capacity, Pyrex, similar to Fisher 5-586.
Harvard trip scale:	2000 gram capacity, 0.1 gram sensitivity for balancing centrifuge bottles.
Safety glasses:	With glass eye pieces (not celluloid or other organic type).

REAGENTS

Sodium peroxide:	Reagent special, Baker and Adamson Code 2273.
Sugar charcoal:	Fisher C-272, finely ground.
Fuse wire:	Parr Cat. No. 45C7.
Sodium carbonate:	Reagent grade.
Nitric acid:	Reagent grade.
Hydrochloric acid:	Reagent grade.
Ammonium hydroxide:	Reagent grade.
Potassium pyrosulphate:	Reagent grade.
Sulphuric acid:	Reagent grade.
Hydrogen peroxide:	Reagent grade.
Mandelic acid (Amygdalic acid, phenylglycollic acid):	16% aqueous solution.
Potassium carbonate:	Reagent grade.
Perchloric acid:	Reagent grade.
Hydrofluoric acid:	Reagent grade.

PROCEDURE

A. Preliminary Treatment

1. *For Refractory Ores, Residues and Other Solid Samples*

(a) *Peroxide Sinter—Caution: wear glasses or goggles.* Weigh a portion of the sample (–200 mesh) containing 10 to 100 mg of zirconium, into a dry platinum crucible, add about five times as much sodium peroxide as ore, and mix thoroughly. Cover the mixture with a little sodium peroxide and heat in a muffle set at 475°C for 7 minutes (4). Remove from the muffle, cool, and using crucible tongs, transfer the crucible to a 600-ml beaker containing about 150 ml of distilled water. Let the melt digest until the mass is thoroughly disintegrated. Remove the crucible with tongs and wash it with about 200 ml of distilled water. Digest the solution on a hot plate for about 30 minutes. Proceed to Section B.

(b) *Peroxide Bomb Fusion Attack*—The sodium peroxide bomb method is described in detail in reference (5), which should be consulted before attempting its use. Weigh a 0.5- to 2.0-gm sample into a fusion cup, add 1.0 gm of finely ground sugar charcoal, 15 gm of sodium peroxide and mix the charge thoroughly. Assemble the bomb, place it in a cooling bath and ignite electrically. After cooling, transfer the cup to a 600-ml beaker containing about 150 ml of distilled water, cover and digest on the hot plate until the mass is thoroughly disintegrated. Remove the cup with tongs, and wash it with about 200 ml of water. Digest the solution on the hot plate for 30 minutes. Proceed to Section B.

2. *Acid Soluble Ores, Precipitates and Metallurgical Products*

Weigh a portion of the ore into a 250-ml beaker, digest on the hot plate with 30-40 ml of 1:1 hydrochloric acid. Add 4-5 ml of nitric acid and evaporate to dryness. Bake at 110°C for 1 hour to dehydrate the silica. Digest the residue with 100-150 ml of 5 percent hydrochloric acid and filter into a 600-ml beaker. Wash the residue and paper with hot water and reserve the filtrate and washings. Transfer the filter paper and residue to a platinum crucible, dry, and burn off the filter paper. Fuse the residue with 5-20 parts of sodium carbonate. Digest the melt in water and filter through a Whatman No. 30 filter paper. Wash the residue with a hot 2 percent sodium carbonate solution and, finally, with a little hot water. Discard this filtrate. Place the beaker containing the reserve filtrate under the funnel and dissolve the residue with 20-30 ml of a 5 percent hydrochloric acid solution. Wash the paper and residue with hot water. Fuse any residue remaining on the filter paper with 1-2 gm of potassium pyrosulphate. Digest the melt in 2-5 ml of sulphuric acid and 1-2 ml of hydrofluoric acid. Evaporate until all the hydrofluoric and most of the sulphuric acid is evaporated and transfer to the beaker containing the reserve filtrate. Add 5-10 ml of hydrogen peroxide to the beaker containing the reserve filtrate, heat somewhat and neutralize with a 10 percent sodium hydroxide solution. Add 5-10 gm of sodium hydroxide in excess and digest for 20-30 minutes on a hot plate. Proceed to Section B.

3. *Solutions Containing Citrates, Tartrates, Oxalates and Other Complexing Agents*

Pipette an aliquot of the solution into a beaker, evaporate to a small volume and destroy the organic material with sulphuric and nitric acids. Perchloric acid should only be used if absolutely necessary, and only after several evaporations with sulphuric and nitric acids have been carried out. *It must never be*

used if hydrocarbons are present. With other organic materials, a mixture of equal parts of concentrated nitric and perchloric acids is recommended and addition of a few milligrams of vanadium salt will catalyze the reaction (7). Safety glasses *must be worn* if perchloric acid is used at all, and a shield covering the whole face is recommended. The operation must be carried out in a hood set aside for use with perchloric acid and on no account should operations involving other organic materials, particularly volatile solvents, take place in or near this hood at any time. Continue as in subsection 4 below.

4. *Solutions, Complexing Agents Absent*

Pipette an aliquot of the solution into a beaker. Dilute to 200-250 ml with water. Add 5-10 ml of hydrochloric and 2-3 ml of hydrogen peroxide. Neutralize with a 10 percent solution of sodium hydroxide and add 5-10 gm of sodium hydroxide in excess. Digest for 20-30 minutes on the hot plate. Omit Section B and continue with Section C.

NOTE: If fluorides and phosphates are absent and the amount of free sulphuric is below 3 percent, the hydroxide separation can usually be omitted. In this case evaporate the aliquot to 25-30 ml, make the solution about 40 percent acid with hydrochloric acid, cool and precipitate the zirconium with mandelic acid as in Section C.

B. Peroxide Separation

If the precipitate is bulky, it should be centrifuged using the procedure described in the next paragraph. If it is small, let it settle and decant most of the supernatant solution through either a Whatman No. 41H or No. 40 filter paper. If the filtrate is turbid, filter again. Discard this filtrate. Add 150-200 ml of distilled water to the precipitate left in the beaker, and digest on the hot plate for 10-15 minutes. Filter through the same filter paper and transfer all the precipitate to the filter paper. Wash the paper and precipitate with a little hot water and discard the filtrate and washings. Place a clean 250-ml beaker under the funnel and dissolve the precipitate on the filter paper with 40 ml of 1:1 hydrochloric acid added in 5-ml portions. Finally wash the paper with 10-15 ml of cold distilled water containing 2 or 3 ml of hydrogen peroxide. Reserve this filtrate and washings.

If the amount of original precipitate was large, it is often advantageous to separate the precipitate from the solution by centrifuging. In this case, transfer solution and precipitate from the 600-ml beakers to 250-ml centrifuge bottles, balance the bottles and centrifuge at 1500 r.p.m. for 15-20 minutes. Decant the supernatant solution through a Whatman No. 41H or No. 40 filter paper and discard the filtrate. Add 150-200 ml of distilled water to the precipitate in the bottles. Break up the precipitate, and centrifuge. Decant the supernatant solution through the same filter paper and discard the filtrate. Dissolve the precipitate in the centrifuge bottles with 40 ml of 1:1 hydrochloric acid and filter through the same filter paper into a clean 250-ml beaker. Finally wash the filter paper with 10-15 ml of cold 3 percent hydrogen peroxide and reserve this filtrate and washings.

Transfer the filter paper from either of the above separations, to the original platinum crucible, dry, ignite and fuse with sodium carbonate. Digest the melt in water and filter through a Whatman No. 40 filter paper. Wash the residue with hot water. Discard the filtrate and washings. Transfer the filter paper and residue to the platinum crucible, dry, ignite and fuse with 1-2 grams of potassium pyrosulphate. Digest the melt in 5-10 ml of 1:1 hydrochloric acid and transfer it to the beaker containing the reserved filtrate and washings.

C. Precipitation

Add 50 ml of a 16 percent aqueous solution of mandelic acid to the combined filtrate, heat slowly to 85°C and digest at this temperature for 20-30 minutes. Filter through a Whatman No. 42 filter paper and wash with a hot solution containing 5 percent mandelic acid and 2 percent hydrochloric acid. Transfer the paper and precipitate to a tared platinum crucible, dry and burn off the paper in a fume hood. Ignite in a muffle at 900°C for 1 hour. Cool and weigh as zirconium oxide, (ZrO_2).

NOTE: If the sample contained large amounts of silica, niobium, tantalum or phosphates or if the ignited zirconium oxide is not pure white, proceed as follows. Fuse the impure zirconium oxides with 5-20 parts of potassium carbonate. Digest the melt in hot water, add a little paper pulp, filter through a Whatman No. 40 paper, wash with a hot 2 percent solution of potassium carbonate and then with a little hot water. Repeat the ignition, fusion and filtration once if niobium predominates, twice if tantalum does. Discard the filtrates and washings. Place a clean 250-ml beaker under the funnel and dissolve the residue with 20-30 ml of 1:1 hydrochloric acid. Wash the filter paper with 10-15 ml of cold water and reserve the filtrate and washings. Fuse any residue remaining on the paper with a little potassium pyrosulphate. Digest the melt with 10-15 ml of 1:1 hydrochloric acid and filter into the beaker containing the reserve filtrates. If a residue still remains, ignite and digest with 2-3 ml of sulphuric acid and 1-2 ml of hydrofluoric acid. Evaporate until all the hydrofluoric and most of the sulphuric is expelled. Take up with a little hydrochloric acid and filter. Wash the filter paper with a little dilute hydrochloric acid. Discard the filter paper. Precipitate the zirconium with mandelic acid, filter, ignite and weigh as zirconium oxide, (ZrO_2).

CALCULATIONS

NOTE: If possible, the weighed zirconium precipitate should be examined spectrographically to verify its purity.

$$\% \ ZrO_2 = \frac{\text{wt. ppt.}}{\text{wt. sample}} \times 100$$

If no precipitate is obtained, the zirconium content should be reported as "less than" the minimum amount detectable. The minimum amount detectable is about 3 milligrams for this method, so that the value to report would be

$$\% \ ZrO_2 = \frac{< 0.003}{\text{wt. sample}} \times 100$$

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