Mines Branch Information Circular IC 134

THE ANALYTICAL DETERMINATION OF URANIUM IN IRON AND STEEL ALLOYS

by

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SYNOPSIS

Recent interest in the use of uranium as an alloying agent for steel has made it desirable for the metallurgical analyst to familiarize himself with the analytical chemistry of this element. This circular summarizes the chemical properties of uranium and reviews current literature for its separation and determination. Typical analytical procedures, illustrating the best-known methods for the separation and determination, and using standard analytical equipment and techniques, are presented. In addition, x-ray and radiometric methods, capable of providing analytical results within a few minutes, are described. The extensive references should be useful in developing new analytical procedures to deal with unusual problems.

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Circulaire d'information IC 134

DÉTERMINATION ANALYTIQUE DE L'URANIUM DANS LES ALLIAGES DE FER ET D'ACIER

par

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RÉSUMÉ

Il y a eu récemment un tel sursaut d'intérêt à l'égard de l'emploi de l'uranium comme agent d'alliage dans l'acier que l'analyste qui s'intéresse à la métallurgie doit maintenant se familiariser avec la chimie analytique de l'uranium. La présent circulaire expose succinctement les propriétés chimiques de l'uranium et donne un aperçu des ouvrages récents qui traitent de la récupération et du dosage de cet élément. On y présente les techniques analytiques caractéristiques, indiquant les procédés les plus connus d'isoler et de doser l'uranium, à l'aide des appareils et techniques classiques d'analyse. De plus, on y décrit les procédés radioscopiques et radiométriques capables de fournir des résultats analytiques en quelques minutes. Les nombreuses références devraient être utiles pour la mise au point de nouveaux procédés analytiques face à des problèmes inusités.

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INTRODUCTION

The discovery of the fissionability of uranium, and the subsequent large-scale development of this discovery for both military and peaceful uses, led to the investigation of its chemical properties on a scale not paralleled for any other element. Almost all those properties that are analytically useful have been exploited, with the result that analytical methods have undergone frequent and extensive changes during the last decade. The literature is vast and excellent reviews have appeared(1)(2)(3)(4).*

This report summarizes those reactions for the separation and determination of uranium which are of interest in connection with the analysis of iron, steel and ferro-alloys. The material is organized in three parts: Part I treats the chemistry of uranium, Part II discusses the separation and determination reactions, and Part III gives a representative collection of analytical procedures.

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*References are listed at the end of the report in the order in which they are numbered in the text.

PART I. THE CHEMISTRY OF URANIUM AND ITS COMPOUNDS

A. URANIUM COMPOUNDS

Uranium forms intermetallic compounds with many metals and also reacts readily with carbon, nitrogen, sulphur and oxygen to form a number of well-characterized products. The chemical properties of these compounds are of analytical importance, firstly, in view of the necessity to obtain all the uranium in the sample in solution form.for the total uranium determination and, secondly, because differences in their chemical behaviour may be of value in permitting the isolation of the compounds responsible for the physical behaviour of the alloys. In so far as compounds with non-metallic elements are concerned, those of particular interest are the oxides UO_2 and U_3O_8, the carbides UC and UC_2, the nitride UN, the sulphides US, US_2 and U_2S_3, and the hydrides. There are, in addition, intermetallic compounds and ternary compounds containing metallic and non-metallic adducts.

The uranium sulphides US, U_2S_3 and US_2 are reported to be very slowly soluble in dilute acids. Uranium nitrides are difficultly soluble in acids and inert to aqueous alkaline solutions. The carbides are said to dissolve only slowly in nitric acid(1). However, a supposedly authentic sample of uranium carbide was found here to dissolve readily in dilute hydrochloric acid (see "Acid-Insoluble Uranium" procedure on page 71 in Part III) and this behaviour is more consistent with other literature onthe subject(5).

Both UO_2 and U_3O_8 are insoluble in dilute sulphuric and hydrochloric acids in the absence of oxidants.

All the uranium oxides are soluble in nitric acid, as are the uranates and diuranates. They also dissolve readily in fuming perchloric acid. Treatment with alkaline peroxide solutions yields soluble peruranates. Uranium oxides and uranium nitrate are soluble in mixtures of glacial acetic acid with nitric acid (20:1) and this reaction has been used to effect a separation from vanadium(6).

The oxides UO_2 and UO_3 do not react with gaseous hydrochloric acid at 400°. The use of hydrochloric acid gas has been investigated for isolating non-metallic compounds from aluminum(7), and in the investigation of titanium sulphides(8), but has apparently not yet been applied in ferrous metallurgy.

Larsen has reported that uranium oxides and certain intermetallic compounds are insoluble in 3 M solutions of hydrochloric acid in ethyl acetate(9). It is not clear from Larsen's paper whether anhydrous or aqueous hydrochloric acid was used in preparing the solvent, and application of this relatively mild reagent to steel analysis has not yet been reported.

Uranium metal and possibly some of the other uranium compounds can be dissolved in 1 M sodium hydroxide -- 5 M hydrogen peroxide mixtures, a fact which might be of use in examining residues from some of the other methods of treatment.

The oxides, nitrides and carbides are insoluble in strong solutions of bromine in ethyl acetate under carefully controlled conditions(9)(10)(11). The same treatment dissolves iron metal and the more easily decomposed sulphides (for example ferrous and manganous sulphides)(12), while the nitrides and carbides of aluminum, chromium, silicon and vanadium(13), the oxides of aluminum, silicon, titanium and zirconium, the more stable sulphides, and carbon remain in the residue with the uranium carbides, nitrides, and oxides(14). Thus the method does not provide a means for isolating the uranium compounds completely. It might, however, be useful for producing a concentrate suitable for study by other means.

There are comparatively few data on methods for dissolving uranium alloys, but such information as is available has been summarized recently by Rodden(15). In general, a method of attack which is capable of dissolving the major constituent is employed first, followed by treatment with an oxidant, such as nitric acid or hydrogen peroxide, to solubilize the uranium.

Many uranium-containing alloys are non-homogeneous, and the uranium-bearing compounds tend to separate toward the portion of the object which was at the bottom during pouring and cooling. This should be borne in mind in sampling such objects, and also in accounting for discrepancies between the amount of uranium added and the amount recovered in the uranium-bearing alloy.

B. SOLUTION CHEMISTRY AND GENERAL SEPARATIONS

1. General

In solution, uranium can exist in four valence states: the trivalent, tetravalent, pentavalent and hexavalent forms. Trivalent uranium forms during the solution of uranium metal. It is powerfully reducing, however, so that it is oxidized by air very rapidly and even by water, though at a slower rate(16). Because of its instability it will not be considered further here. Similarly, pentavalent uranium appears only fleetingly during transitions between the tetravalent and hexavalent states. It is of interest chiefly in connection with polarographic methods(17).

The two stable states, tetravalent and hexavalent, are analytically important for several reasons. Existence of the two forms permits the use of oxidation-reduction methods for volumetric determinations; each form has distinctive compounds suitable for determination by a variety of techniques; and transition from one form to the other facilitates some separations.

2. Uranyl Ion

Uranium VI does not exist in solution alone, but in the form of the UO_2^{2+} ion. This is the most stable valence state and uranium in this form can be separated easily from tetravalent ions (e.g., Th, Ti, Zr) and many others. It forms soluble complexes with a number of inorganic ions, such as carbonate, chloride, nitrate, fluoride, sulphate, sulphite and thiocyanate, which are useful both in ion exchange separations and also for masking uranium during the course of the separation of other elements. The uranyl nitrate complex is soluble in many simple oxygenated solvents and many of the other forms are solvent-extractable using the organic phosphates and organic amines.

Uranyl phosphate is soluble in acid solution, but precipitates as the pH is raised. Hydrolysis of uranyl ion (by addition of metal or ammonium hydroxides) proceeds by a "chain-and-links" mechanism to produce a large number of imperfectly characterized "salts" called uranates. Presence of high concentrations of carbonate delays the onset of precipitation, by complex formation, so that the precipitate produced by addition of sodium hydroxide to a carbonate solution has a unique composition. Hydrogen peroxide precipitates uranium from solutions of uranyl ions in acid solution (a reaction which is no longer used analytically), but in alkaline solution it produces soluble peruranates, providing a colorimetric method, a convenient separation, and a useful masking device. The complex uranyl sulphates and chlorides find their principal application in ion exchange and solvent extraction separations.

Uranyl ion reacts with many organic reagents. It forms stable complexes with acetate and other aliphatic acid anions, and with oxalate and malate. Similar compounds are formed with aromatic acids such as salicylic and sulphosalicylic acids. With certain other organic compounds it forms solvent-extractable species. These include the disubstituted dithiocarbamates, the 1, 3-diketones, 1 nitroso-2 naphthol, and 8-hydroxyquinoline.

The fact that most of its salts with organic and inorganic anions (such as sulphate, fluoride and oxalate) are soluble permits the separation of uranium from elements forming insoluble compounds under the same conditions. The uranyl cupferrate is soluble and not extractable, providing a separation from vanadium, iron, titanium, tantalum and zirconium (niobium cupferrate precipitates also, but is not soluble in chloroform and must be filtered off(18)). This reaction is discussed further in Part II.

Uranyl ion does not precipitate with tannin in weakly acid oxalate solution half-saturated with ammonium chloride, under which conditions, niobium, tantalum, titanium, tungsten and tin can be eliminated(19). In buffered acetate solution, uranium is precipitated by tannin; tartrate and carbonate do not interfere(20).

In spite of its great tendency to participate in the formation of complex ions, the uranyl ion reacts only weakly with ethylenediamine tetraacetic acid(21). This fact is of great utility since many common interfering ions form strong complexes under similar conditions. These include iron, chromium, cobalt, copper, nickel, bismuth, zinc, vanadium, cerium and thorium (but not titanium or beryllium). The complexing agent has been used both in gravimetric(22) and in colorimetric analysis(23).

3. Uranous Ion

Uranyl ion is easily reduced to the uranous form, U IV, by a number of metals, amalgams and inorganic reductants, and can also be reduced electrolytically. In solution the ion exhibits a deep, apple-green colour and has strong absorption peaks at 650-680 mμ. Its chemical properties parallel those of thorium in a striking manner. Thus, uranium IV oxalate precipitates in weakly acid solution but tends to redissolve as the pH is raised, and forms a stable soluble complex $(U(C_2O_4)_4)^{4-}$ in neutral solutions. It is strongly complexed by sulphate ion and forms a carbonate complex,which, like that of thorium, is stable over a slightly more restricted pH range than that of the uranyl tricarbonate complex. Tartaric and nitric acids also form complexes with the ion. Uranous ion is precipitated by fluoride and iodate salts, and by cupferron. The uranium IV cupferrate is soluble in chloroform or ether, and this reaction has been used extensively to separate uranium from chromium, manganese, nickel and cobalt, after a preliminary removal of iron, titanium, vanadium and other impurities while the uranium is in the uranyl form(24).

However, the chief analytical interest in the chemistry of the uranous ion derives from its use in connection with volumetric oxidation-reduction methods for determination of the element, and the aspects relating to the determination are discussed in Part II under the heading, "Volumetric Methods" (page 32).

PART II. THE SEPARATION AND DETERMINATION OF URANIUM

A. METHODS OF SEPARATION

In Part I, the solution chemistry of uranium has been described briefly in general terms. Some of the important separations, which could be of value in the analysis of complex alloys, will now be considered in detail.

1. Precipitation Methods

Precipitation methods are seldom used, but in special cases may offer advantages. Some have already been met in the previous discussion on the chemistry of the uranium. The most commonly employed procedure involves the use of ammonia to separate uranium from nickel, copper, cobalt, manganese, cadmium and zinc. It also provides a means for eliminating sulphate after (for example) a mercury cathode separation, when sulphate could interfere in subsequent steps of the method. Precipitation is carried out from hot solution, carbonate must be absent, and for small amounts of uranium a little iron or aluminum must be present to act as a collector.

The use of EDTA to improve the separation, and eliminate iron and aluminum as well, has been reported(25). The problem of finding a suitable collector would be difficult in the application of this technique to precipitation of small amounts of uranium.

Modifications in which pyridine replaces ammonia as a precipitant are reported to give cleaner separations(26).

Uranium can be separated from many interferences by precipitation as the phosphate in the presence of EDTA. Iron, chromium, copper, nickel and vanadium are not precipitated(27).

Titanium and beryllium (and possibly the earth acids) precipitate with uranium, although addition of a few drops of hydrogen peroxide prevents interference of small amounts of titanium. The gelatinous nature of the uranous phosphate precipitate leads to coprecipitation and entrainment of impurities, and to difficulties in filtering and washing. Although this precipitation was reported originally for the gravimetric determination of uranium (the precipitate is ignited to pyrophosphate), it would appear to have advantages as a separation step in steel analysis, provided that phosphate ion, the removal of which is difficult, is not deleterious in subsequent steps.

The cupferron precipitation of tetravalent uranium has been recommended for isolating uranium for gravimetric determination(28), the step usually being employed after precipitation of other elements with cupferron while uranium is in the uranyl form(24). With small amounts there is a tendency for the uranous uranium to be re-oxidized and thus fail to be precipitated. The preliminary cupferron precipitation of impurities from a solution containing uranium in the uranyl form is an extremely valuable tool. It will be discussed further in the section on solvent extraction, but is included here because if niobium is present the separation is carried out by filtration, due to the insolubility of niobium cupferrate in common organic solvents(29). The complexing agent EDTA has also been used in conjunction with cupferron(30).

A precipitation from boiling solution using alkali carbonate is often employed to separate iron and aluminum from uranyl ion which remains in solution as the tricarbonate complex. This method is usually not recommended, the principle faults being extensive co-precipitation of uranium, and difficulty in filtering and washing the precipitate. Brackenbury(31) and Upor(32) report the use of copper and thorium, respectively, to assist in overcoming both problems.

Uranium can be precipitated with oxine (8-hydroxyquinoline). If this is carried out in the presence of EDTA, separation from iron, copper, cobalt, nickel, manganese and phosphate is possible(22).

Separations employing tannin have already been discussed in Part I (page 7). Their principal application would be in connection with the determination of uranium in high-niobium alloys. In this connection, our experience has been that, contrary to many statements that appear in the literature, the ordinary hydrolytic precipitates of niobium--which are encountered when dealing with moderate amounts of niobium--do not entrain uranium if sufficient nitric acid is present. For this reason, it will seldom be found necessary to employ tannin.

2. Electrolysis Methods

Many elements can be separated from uranium by depositing them electrolytically on metallic electrodes. The most useful method employs the mercury cathode(33). By this means, uranium is quickly and quantitatively separated from iron, chromium, nickel, copper, cobalt and molybdenum. As much as 4 grams of iron, nickel or copper can be removed in 1/2 hour using the commercial high-current apparatus(34), although the removal of the last traces of iron by this method is usually not practical. The principal disadvantage is that the electrolysis is usually carried out in a very dilute sulphuric acid solution, and sulphate may interfere in the subsequent determination. The use of a perchlorate medium would eliminate this problem. Uranyl ion is quantitatively reduced to the uranous form and may require to be oxidized before further treatment.

3. Solvent Extraction

Extraction of Uranyl Nitrate

Probably the simplest and most satisfactory analytical separation of uranium from other elements, for its determination, is obtained by extraction of the uranyl nitrate from aqueous nitrate solutions, using oxygenated organic solvents. Typical solvents are ether(6), methyl iso butyl ketone (hexone)(35), "penta ether" (dibutoxy tetraethylene glycol)(36), and ethyl acetate(37). Tributyl phosphate has also been used(38).

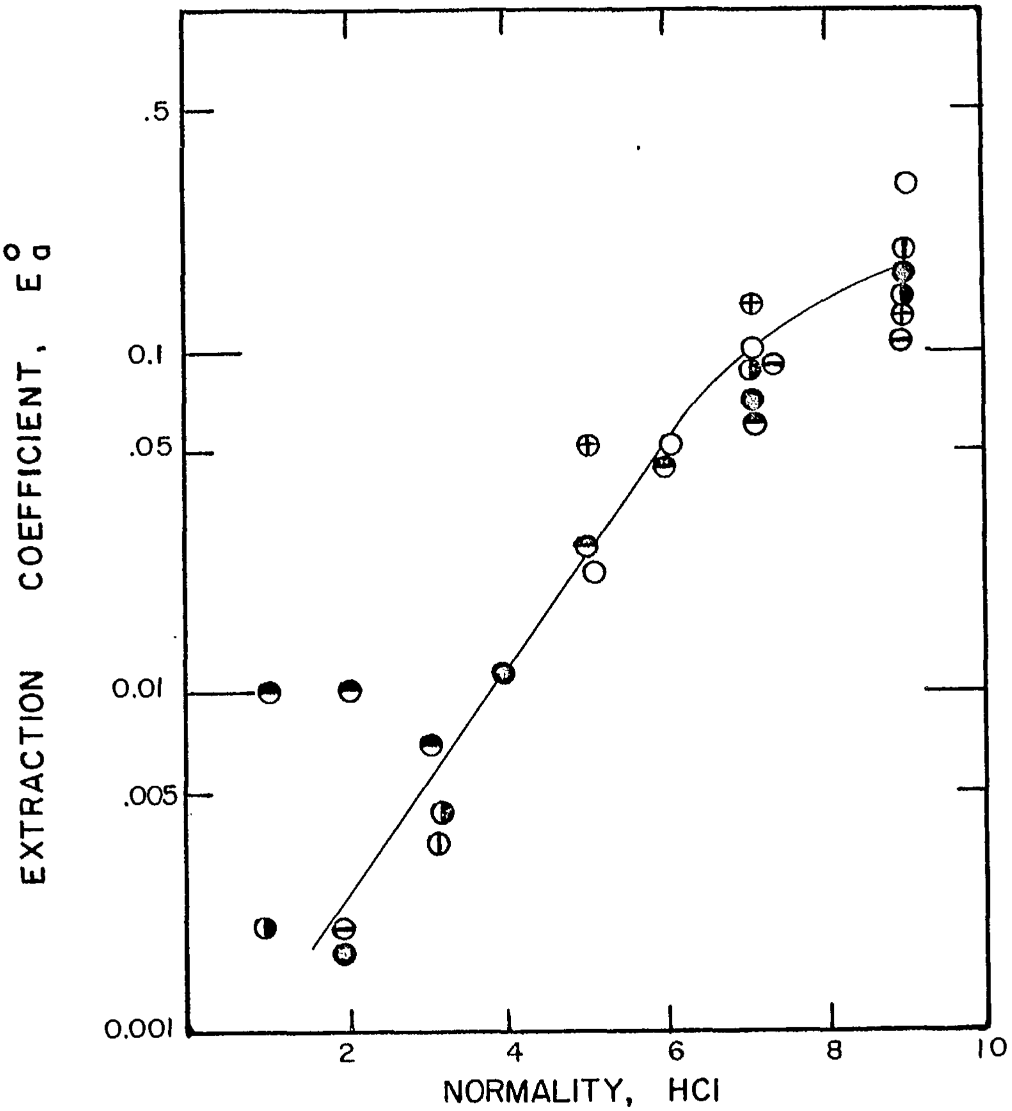
In all cases the separation is improved if a "salting agent" is used. Ferric nitrate and aluminum nitrate are both effective for the purpose. The "salting agent" serves the purpose of providing the excess nitrate ion needed to depress the ionization of uranyl nitrate and hence promote formation of the solvated complex. At the same time the ability of the metal ion to bind water molecules reduces the "free" water concentration in the aqueous layer, preventing the formation of "aquo" complexes, which again favours the solvation reaction. A further function served by these particular metal ions is to bind sulphate, phosphate and fluoride ions, which otherwise would complex uranyl ion and prevent quantitative recovery of uranium.

The most generally desirable of the above solvents is ethyl acetate, from the standpoint of both its physical and its chemical characteristics. It is less flammable than ether; phase separation is better than with most of the other solvents; and uranium is easily stripped from it with water. Studies in this laboratory have shown that 20 ml of ethyl acetate will quantitatively remove up to 200 mg of U from 11.5 ml of a solution 2.5% in nitric acid, containing about 10 grams of aluminum nitrate enneahydrate. The uranium is separated completely from relatively large amounts of vanadium, iron, molybdenum, copper, nickel, cobalt, manganese and chromium. Interestingly enough, large concentrations (up to 3 N) of chloride ion do not prevent the extraction of uranium if the salting agent concentration is maintained(39).

At this level, one would expect some iron to be extracted(40), but the presence of, say, 1 N chloride ion concentration should cause little difficulty (see Figure 2, on page 18). If a rapid analysis were required then, a sample could be dissolved in aqua regia and the analysis continued without removal of hydrochloric acid.

Separation by Extraction of Ferric Chloride with Organic Solvents

The extraction of ferric chloride from strong hydrochloric acid solutions by organic solvents is a well-known and frequently used separation in steel analysis. Various ethers and esters have been employed. Ethyl acetate is used for this purpose in our laboratory, and extraction coefficients ([concentration, g/l in organic]/[concentration, g/l in aqueous]) of iron and uranium between this solvent and hydrochloric acid of various concentrations have been determined here. The values of these coefficients for the commonly expected uranium and iron concentrations are presented graphically in Figures 1 and 2. The extraction of uranium (Figure 1) is low, but increases with increasing hydrochloric acid concentration. Values at any one acid concentration are the same, regardless of uranium concentration. Iron extraction, on the other hand, is strongly influenced both by the hydrochloric acid concentration and by the iron concentration. The effect is due to the multiplicity of chloro complexes formed by ferric iron. From the practical point of view, the figures suggest that, when it is desired to remove the iron from a concentrated ferric

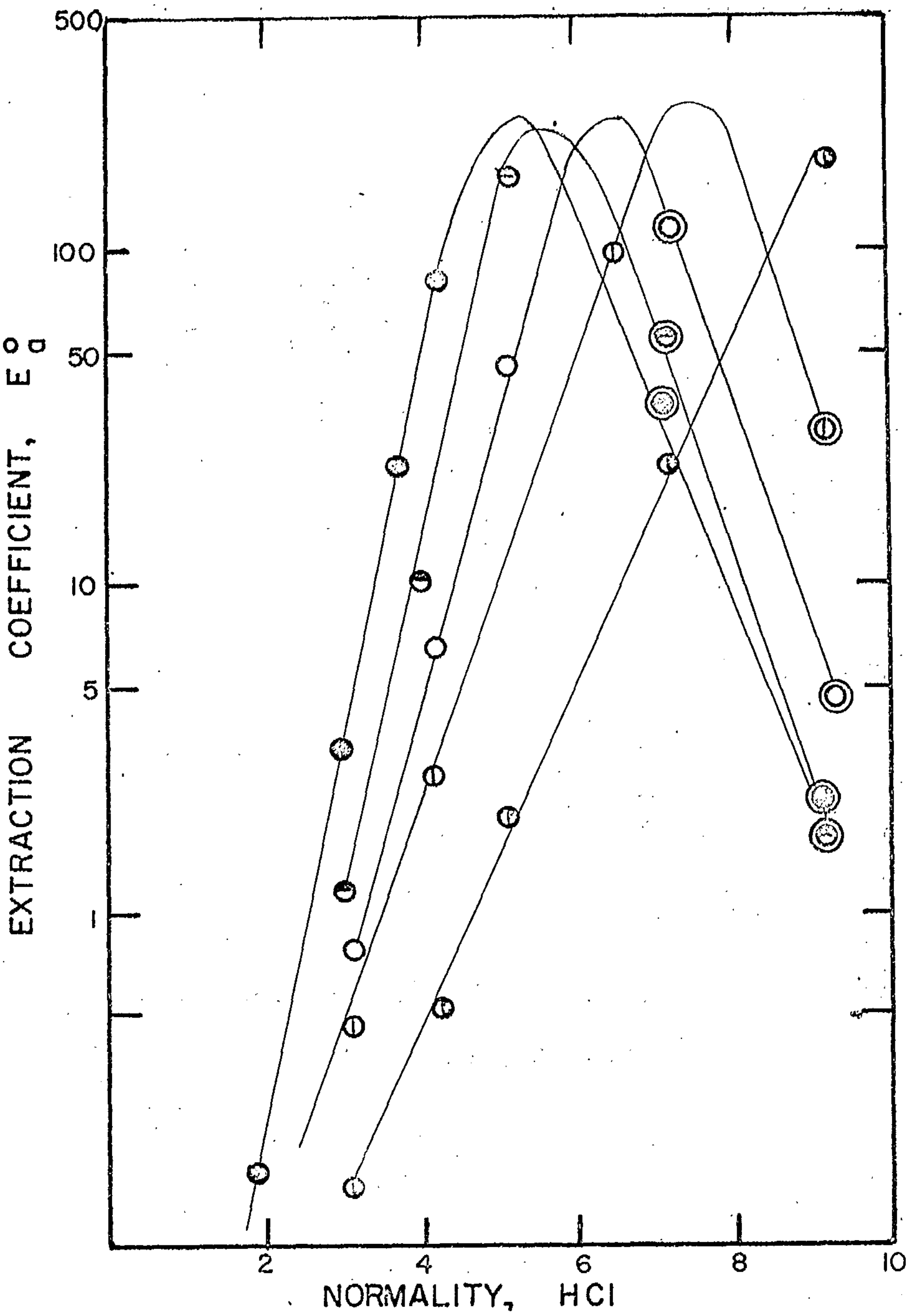


Original U_3O_8 Concentration in Aqueous Solution:

○	0.001 g/l	⊖	1 g/l
◒	0.01 g/l	⦶	5 g/l
◑	0.1 g/l	◍	10 g/l
⊕	0.5 g/l		

Phase Ratio, organic to aqueous, 30:1.

Figure 1. Extraction of uranium by ethyl acetate from hydrochloric acid solutions.



Original Fe Concentration in Aqueous Solution

◍ 0.1 g/l
⊖ 1.0 g/l
○ 5.0 g/l
⊖ 10.0 g/l
◐ 20.0 g/l

Phase Ratio, organic to aqueous, 30:10.

NOTE: Circled points indicate high solubility of organic phase in aqueous phase.

Figure 2. Extraction of iron by ethyl acetate from hydrochloric acid solutions.

chloride solution, the preliminary extraction should be carried out from a solution 8M in hydrochloric acid, followed by a second extraction after the aqueous phase has been diluted, say to 4M, by the addition of an equal amount of water. A second reason for employing this technique is that the organic solvents tend to be miscible with the stronger acid once the bulk of the iron is removed. The paper by Tadashi(40) presents further useful information on this separation.

Similar data with respect to ether extraction of uranium from chloride solutions have not been reported although Kern found macro amounts were not extracted(41). Troitskii(42) reports a very similar study of the system ferric chloride-ether.

Cupferron Extraction

A number of interfering elements such as iron, vanadium, titanium, molybdenum and stannic tin react with cupferron in moderately strong acid to form solvent-extractable precipitates. Tetravalent uranium also extracts, so that all the uranium must be oxidized if the method is to be used(18). The separation is extremely valuable and is extensively employed.

The Beta Diketones

The beta diketones (e.g., acetylacetone, thenoyl trifluoroacetone) are useful reagents for uranium separations. Because of their application in colorimetry, they are discussed later herein, under "Methods of Determination" (see page 29).

Di-alkyl Dithiocarbamates

The substituted dithiocarbamates react with many metals, including uranium, to form colored, solvent extractable precipitates(43).

The uranium salt is soluble in chloroform, ethyl acetate, and methyl isobutyl ketone, but not in carbon tetrachloride, which latter solvent dissolves a number of other di-alkyl dithiocarbamates. Moreover, it forms over a relatively narrower pH range than do the salts of many other elements. These facts, plus the possibility of masking, suggest that the reagent might be quite useful in steel analysis when uranium is present.

Organic Phosphates, Phosphonates and Phosphine Oxides

No discussion on uranium separations would be complete without mention of the various organic phosphorus compounds, which have been widely used for preparing nuclear-grade uranium compounds and for the treatment of spent nuclear fuels. Tri-butyl phosphate was the first of these(44), and its properties have been studied intensively(45). This reagent, and the other phosphorus compounds, are usually employed as solutions in organic diluents, although in special cases the pure reagent has been used. A nitrate system is the most generally useful, but interesting separations are possible in hydrochloric acid media(46).

The success obtained with tributyl phosphate led to a study of its homologues, the tri-alkyl phosphates, and of other similar series of homologous phosphorus compounds, the mono-and di-alkyl phosphoric acids, the di-alkyl alkyl phosphonates and the phosphine oxides(47)(48). The phosphine oxides are extremely effective uranium extractants and can extract it from sulphate and phosphate solutions where tri-butyl phosphate is useless. Indeed, these compounds are, potentially, extremely useful in analysis, and one of them, tri-octyl phosphine oxide, has been the subject of a great deal of recent research(49).

Amines

One of the most recent developments in methods for separating and isolating uranium from mixtures of other elements is the use of long chain alkyl amines(50)(51). These reagents, which are used as dilute solutions in various organic solvents, are, in effect, liquid anion exchangers, and the mechanism involved is similar to that occurring with the solid, resinous ion-exchange materials. The manipulations of solvent extraction are simpler and more rapid than those of solid-phase ion exchange, which is desirable for analytical procedures. Moreover, the variety of these compounds available, including primary, seconday, and tertiary amines, as well as the quaternary ammonium compounds, combined with an even greater choice of alkyl substituents, leads to a wide range of possible reagents, many with unique properties. A sulphate medium is most commonly used for uranium extraction, but, in general, any system finding application in conventional anion-exchange has a counterpart in amine extraction methods(52)(53). The carbonate system is a possible exception, for, although some quaternary ammonium compounds extract uranium from these solutions, separations are poor and the extraction is unsatisfactory in many ways(54). It is impossible within the scope of this report to discuss the many applications of amine extraction to uranium separations and the reader is directed to the references for further details.

4. Ion Exchange Separations

There is a large variety of possibilities for separating uranium by ion exchange, and both anion and cation exchange have been used.

With anion exchangers, the following media have been employed: sulphate(55); hydrochloric acid(56)(57); ammonium, aluminum and nickel nitrates(58)(59)(60); acetate(61); ascorbate(62); and carbonate(63).

Cation exchange has been employed by a number of investigators, the principal variation being in the eluant used to effect the separation(64)(65)(66).

Fodor describes the use of EDTA in the sample solution to prevent the absorption of ions other than uranium by the resin(67).

A fairly extensive review on the ion exchange behaviour of uranium has appeared recently and should be consulted for further details(68).

In general, ion exchange methods are more time-consuming than other analytical techniques. They have unique advantages for many separations, however.

B. METHODS OF DETERMINATION

1. The Fluorimetric Method

The brilliant fluorescence obtained when uranium, fused into beads of sodium fluoride, is illuminated with ultra-violet light, forms the basis of a sensitive and specific method for its determination(69).

The fluorescence output is a linear function of concentration over a wide range. Large amounts of certain elements, called quenchers (many of which are found in steel), can reduce the fluorescence. Small amounts of them can be tolerated by working with smaller amounts of uranium, since the quenching effect is a function of the quencher/flux ratio. "Spiking" has also been proposed but is usually ineffective. Many groups have investigated these effects and details will be found in the references (70)(71)(72)(73).

As a rule, not more than 2 micrograms of iron can be present in the final aliquot, and since the quantity of uranium usually measured is about 0.1 microgram, a prior separation will be required in steel analysis. The ethyl acetate extraction of uranyl nitrate provides one of the most convenient separations.

The instrument used to measure the fluorescence plays an important part in determining the accuracy of the results obtained. In particular, the level of stray ultra-violet light controls the ultimate sensitivity and linearity of response. Reflection of this stray light has been found to be highly dependent on the reflectance of the fusion dish and on the translucence of the fused bead. This can lead to differences between the readings obtained with standards and with samples of the same uranium content. The effect is largely overcome by using a special flux (98% sodium fluoride-2% lithium fluoride)(74), in conjunction with fusion dishes of platinum-rhodium alloy. The combination permits easy removal of the fused beads so that they can all be read against the same background.

The fusion is most satisfactorily carried out over a gas flame, the burnt gas atmosphere preventing solution of platinum in the flux, which would cause quenching. A Fletcher radial flame burner, using compressed air, is satisfactory and permits fusion of 22 beads under roughly identical conditions. Recently, many workers have switched to a ring of about 12 Fisher Meker burners, over which the fusion dishes are rotated mechanically a number of times during the course of the fusion step(75)(76). This system has the advantage that compressed air is not required, the fusion step can be fully automated, and all the dishes are exposed to substantially the same fusion conditions.

The precision of the fluorimetric determination is relatively constant over the usual alloying range, and typical values are given in Table 1.

TABLE 1

Precision of the Fluorimetric Method for the Determination of Uranium in Steel: Typical Values

Uranium Content (%)	Standard Deviation	Coefficient of Variation
0.034	0.0019	5.5
0.050	0.0028	5.6
0.087	0.0021	2.5
0.111	0.0033	3.0
0.118	0.010	8.6
0.137	0.0063	4.6
0.520	0.021	4.1

2. Spectrophotometric Methods

Direct Determination

Uranium ions in all their valence states are coloured, the trivalent form being red (dark green under fluorescent light), the tetravalent form apple-green, and the uranyl ion yellow. The first two have the more intense colour, but are too unstable for routine use. The uranyl ion itself exhibits only weak absorption and, though the sensitivity is improved in carbonate and sulphate media as a result of the increased absorption of the corresponding complex ions, the colours are, in general, only useful for the determination of high concentrations of uranium.

Alkaline Peroxide Systems(1)

The yellow colour due to the peruranate ions is not intense, but can be made extremely reproducible, and the colour is very stable provided that ions which cause catalytic decomposition of peroxide are absent. The intensity increases as wavelength decreases, but below 400 mμ blank absorption becomes a factor. The highest practical sensitivity is obtained at 370 mμ. Either carbonate or hydroxide systems can be used, but the latter is preferable and is the one discussed here.

Manganese and iron interfere by precipitating and occluding uranium, and by catalyzing decomposition of the peroxide. Copper and nickel, even in trace amounts, cause rapid decomposition of peroxide, interfering both by reducing the colour and by producing objectionable gas bubbles. Molybdenum can cause high results, but the effect is reduced by letting the solution stand for 4 hours.

Chloride, nitrate and sulphate do not interfere. Phosphate above 10 g/l, silicate above 0.6 g/l, and fluoride above 0.1 g/l, all cause bleaching of the colour. Chromate and vanadate interfere seriously, although boiling and cooling the solution will destroy the vanadate colour.

The influence of many cationic interferences can be eliminated by the use of nitrilotriacetic and tartaric acids and by reading the colour at 400 mμ (23).

Thiocyanate Systems

In moderately strongly acid solution, thiocyanate reacts with uranium to give an intensely yellow-coloured compound(77). The concentration of the coloured complex is a function of the thiocyanate concentration, which must be controlled to obtain reproducible results. It can be developed in organic media, such as acetone(78), ethyl acetate-acetone(79), methyl ethyl ketone(80), and methyl isobutyl ketone-butyl cellosolve(35).

The thiocyanate colour can also be developed in the aqueous medium and then extracted into an organic solvent, such as amyl alcohol or ethyl ether(81), penta-ether(82), or tributyl phosphate in carbon tetrachloride(83).

Many elements interfere in the direct thiocyanate determination. These include ferric iron, molybdenum, vanadium, titanium, niobium, cobalt, lead, chromium, nickel, zirconium and possibly bismuth. The interference of moderate amounts of ferric iron is eliminated by reducing it with stannous chloride(77) , thiosulphate(78), 1-ascorbic acid(84)(85), or by complexing it with EDTA(83).

It is necessary to isolate the uranium from the other impurities by separation procedures. The separation most used is solvent extraction of uranyl nitrate. In general, the modifications in which the colour is developed directly in the solvent phase offer few advantages and are somewhat messy to use. The direct extraction of the uranyl thiocyanate can be even less advantageous. However, the modification described by Clinch and Guy(83), whereby the coloured complex is extracted by tributyl phosphate from an aqueous medium in which most of the above interfering ions have been complexed by EDTA at controlled pH, has a number of desirable features. These include simplicity, speed, and high sensitivity. Molybdenum, tungsten and cobalt still cause interference, however, that due to molybdenum being the most serious.

The procedure given in Part III uses conventional separations and the simple thiocyanate procedure. Few elements commonly found in steel alloys are likely to cause difficulties with it.

Azide Systems

The azide ion, N_3^-, behaves in many ways like the thiocyanate ion, and gives similar colours with iron and uranium. Its use for the determination of uranium has been investigated(86), the colour being said to be somewhat more intense and more stable than the corresponding thiocyanate colour. However, azides are poisonous and their metal salts are high explosives. Hydrazoic acid has about the same physical properties and toxicity as hydrocyanic acid, and the use of a 3 M solution of azide in approximately 0.5 M nitric acid would appear to involve some risk.

The Beta-Diketones

The 1, 3 diketones are a group of organic analytical reagents of great analytical utility, both for separations and for colorimetric determinations. The most generally useful are acetylacetone, thenoyltrifluoroacetone and dibenzoylmethane, and all three have been used for uranium determinations. The use of acetylacetone was recently investigated by Tabushi(87). Thenolytrifluoroacetone was used by Khopkar and De(88), and its behaviour with most of the elements of the periodic table has been summarized(89)(90).

Dibenzoylmethane, however, has received the most attention, since first being reported by Yoe et al. in 1953(91). This is not surprising, since it is one of the few colorimetric reagents that permit an approach to the sensitivity of the fluorimetric method. The list of interferences is somewhat awesome, however. The colour can be extracted into organic solvents similar to those used with thiocyanate, and in general the separations and masking techniques employed are similar. Details of the techniques will be found in the references(92)(93)(94).

Similar reagents, 2 furoyl trifluoro acetone(95) and p-carboxy dibenzoyl methane(96), have recently been reported to be even more sensitive than dibenzoylmethane.

Because of the necessity to eliminate interferences almost completely, dibenzoylmethane is not widely used in the determination of uranium in ores. In the case of determination of uranium in a specific steel alloy, where a separation might be relatively simple, it may offer very real advantages.

O-arseno-o-hydroxyazo Compounds

Compounds of this type were synthesized by Kuznetsov and investigated by him as reagents for many elements(97). They have proven particularly valuable in the determination of the lanthanides and the actinides. Fifteen such compounds are described in a recent publication(98). The most useful to date have been "thoron" (thorin, thoronol, naphtharson); 2-(2 hydroxy -3, 6 disulpho-1 naphthyl azo) benzene arsonic acid; arsenazo (neothorone); 3-(2-arsonophenylazo) -4, 5-dihydroxy-2, 7 naphthalene disulphonic acid; "arsenazo II", biphenyl -4, 4'-diarsonic acid -3, 3'-bis<azo-2>-1, 8-dihydroxy-naphthalene -3, 6-disulphonic acid; and "arsenazo III", 1, 8-dihydroxy-naphthalene -3, 6 disulphonic acid -2, 7-bis <azo-1> 2 phenylarsonic acid.

"Thoron" is so called because it is fairly selective for thorium. Since tetravalent uranium behaves very much like thorium, it gives a colour with this reagent, which forms the basis for a highly sensitive method(99). The colour is developed in the presence of acetone in moderately acid medium after reduction of the uranium by a lead reductor. Iron, chromium, vanadium, copper, manganese and molybdenum, along with zirconium and cerium, interfere. Phosphate, nitrate, sulphate and fluoride should be absent.

"Arsenazo" is a somewhat more versatile reagent and its use for the determination of 14 elements in addition to the rare earths has been reported(100). It reacts with both uranous and uranyl ions (under different conditions) and the uranyl ion reaction has been investigated for uranium determination by a number of workers(101)(102)(103)(104)(105)(106). It is even more sensitive than "thoron". The stable blue complex forms instantaneously, is quite stable, and its absorbance peak at 590 mμ is well separated from that of the reagent. Control of pH is fairly important, and use of a buffer solution is recommended. Most elements found in steel alloys interfere, although quite large amounts of fluoride are permissible, suggesting that masking techniques can be employed.

Recently, both arsenazo II(107) and arsenazo III(108)(109) have been proposed as uranium reagents, the latter being said to provide a highly specific method for uranium.

PAN Reagent

The reagent 1-(2-pyridylazo) naphthol was first proposed as a complexometric indicator by Cheng and Bray(110), and was subsequently found to be a sensitive reagent for uranium(111).

Several methods employing it have appeared recently(112)(113).

These methods permit a broad latitude for most of the elements found in steel, and probably a simple mercury cathode separation would be the only preliminary treatment required in most cases.

3. Volumetric Methods

In the usual volumetric methods for uranium, the ion is reduced to the uranous form by a suitable reductant, and then either titrated directly with an oxidant or allowed to reduce ferric ion and the resulting ferrous iron titrated. Reduction can be accomplished by means of a column containing amalgamated zinc(114) or lead(115). Normally, a 2% amalgam zinc reductor is used, but when the solution contains nickel a 10% zinc amalgam must be used to prevent poisoning(116). With the solid zinc amalgam reductor, trivalent uranium is produced(16). Ordinarily this is converted to tetravalent uranium by a short aeration treatment, although if copper is present some uranyl ion will be produced. Other solid reductants have been employed, e.g., cadmium amalgam(117) and silver, lead and zinc metals. Liquid amalgams have been employed, and liquid zinc amalgam has the advantage that tetravalent uranium only is obtained(118). Other reductants used are stannous chloride(119) and titanous sulphate(120)(121).

The reduced uranium may be titrated directly with potassium permanganate, with ceric sulphate, with potassium dichromate, or with a solution of a ferric salt.

The end point is improved in the ceric sulphate titration if an excess of ferric sulphate is added to the uranous solution and the resulting ferrous iron is titrated; and this modification is essential if potassium dichromate is used as titrant. Titration with ferric salt is interesting, because in this case a relatively large amount of iron can be tolerated in the reduced solution. It has not found favour because a potentiometric end point has to be used and the solution must be titrated hot due to the slowness with which equilibrium is established at room temperature(122). Recently it has been suggested(123) that the reaction itself occurs very rapidly in the cold and it is the sluggishness of the end-point indicating system that necessitates the high temperature. This view is not universally held and various aspects of the problem have been considered by Desai(124) and Sagi(125).

The volumetric method is used extensively for the determination of small amounts of uranium on the Colorado Plateau(115). A modification of the method, said to be less time-consuming for samples high in iron, is the subject of a current report(126).

4. Coulometric Methods

Recently a number of coulometric methods for uranium have appeared. In some of these, the uranium is "titrated" with electrolytically generated reagents, the end-point being determined by various electrical measuring systems, amperometric(127), potentiometric(128), and derivative polarographic(129). In one case, uranous ions are used to reduce ferric ions, and the ferrous ions produced are "titrated" with ceric ions. In another, uranous ions are titrated with bromine in the presence of excess ferrous ions. In a third case, uranyl ion is reduced with titanous ions. In all these methods the amount of "titrant" used is determined from current-time measurements.

A direct coulometric approach has been employed by Booman et al. (130)(131). In this procedure, the current required to reduce uranyl ion to uranous ion in citrate medium at the mercury cathode, using a controlled potential of -0.60 volt, is measured. Interference of small amounts of copper and iron is eliminated by pre-reduction at -0.20 volt (potential values are referred to the silver-silver chloride:saturated potassium chloride electrode). The method is said to permit the determination of as little as 7.5 micrograms of uranium with very high precision. It was found here that cell geometry was highly critical. The equipment is specialized and expensive.

5. Polarographic Methods

Uranyl ion is reducible at the dropping mercury electrode, and polarographic methods are often recommended for the determination. In mineral acids, a two-step reduction occurs, but because of the many interferences these media are not often used. By using supporting electrolytes containing reagents that complex uranium, however, the half-wave potentials can be shifted to regions relatively free of interference, and the method is attractive for specific problems. Choice of a suitable electrolyte will be governed by the nature and concentration of the elements accompanying uranium, and the references given should aid in deciding on a suitable medium. In general, the bulk of the iron must be removed, the choice of method being governed partly by the electrolyte composition chosen(132)(133) (134)(135)(4).

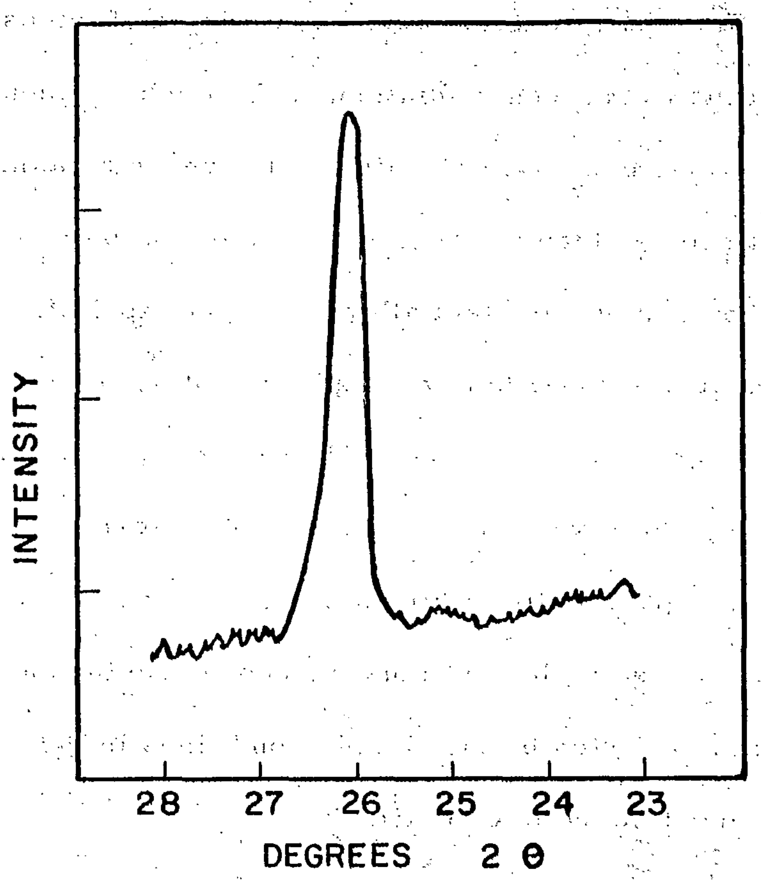
6. Optical Spectrographic Methods

The optical spectrograph has been used occasionally for uranium determinations. Strasheim(136) used the 4244.4 A line and the Fe 4238.8, Fe 4247.4, V4232.5 or V 4238.4 lines as internal standard lines. He also investigated chromium and titanium as internal standards. His techniques included direct evaporation of the sample in a D. C. arc using graphite as a stabilizer, a similar method in which lead chloride was employed as an enhancing agent, and a method involving a prior concentration of the uranium. Warfield(137) used a similar technique but found the results not very reproducible. Burgener(138) reported a sensitivity down to 0.03% on ores, using a mixture of magnesium chloride and palladium chloride as a buffer in the D. C. arc. The spectrograph is not, however, entirely suitable for the determination of small amounts of uranium.

7. X-ray Spectrometry

The secondary x-rays emitted by an element when excited by primary high energy x-radiation provide the basis for a very convenient method for determining uranium. The principles on which the method is based have been known for a very long time, but it is only within the last decade that conveniently-operated apparatus has become available. In this method, a sample is irradiated with high energy x-rays from a suitable x-ray tube. The radiation ejects electrons from the inner K or L shells, and outer electrons moving into the vacancies so created, give rise to photons whose wavelengths (also in the x-ray region) are a function of the energy differences between the electron orbits in the respective shells. The emitted x-rays are analyzed by directing them in a collimated beam onto an analyzing crystal, the atomic planes of the crystal lattice acting as a diffraction grating. By this means, radiation of different wave-lengths is directed away from the crystal at an angle related to the wave-length by the Bragg equation. A radiation counting device, mounted on an accurately-divided movable goniometer arm, measures the intensity of the radiation and either plots the data as a function of angular position or can be set at a particular angle to determine the intensity of fluorescent radiation of a particular wave-length.

The intensity of the secondary radiation is dependent, among other things, on the energy of the primary radiation, but in a discontinuous fashion. That is, the energy of the primary radiation must exceed a certain value, called the absorption edge, before an electron can be ejected from a particular orbit. Each element has a series of absorption edges, for the M spectrum, the L spectrum and the K spectrum. The K spectrum is the simplest and is used by preference, but in the case of uranium a minimum voltage of 115 kv on the x-ray tube is necessary to excite these lines and this is not attainable with readily available equipment. Hence one of the L lines is used. A typical x-ray spectrometric trace is shown in Figure 3.



Sample : Stainless steel, 12% Ni, 18% Cr, 0.53% U.
Dilution : 1:1 with Al_2O_3.
Excitation: 50 kv, 30mA.
Crystal : Lithium fluoride.

Figure 3. X-ray spectrometric trace of the uranium L_α line.

The x-ray fluorescent emission is complicated by many factors relating to the composition of the sample. These are called "matrix effects". They may consist both of a reduction of intensity due to absorption of the fluorescent radiation, and an enhancement effect caused by selective excitation of a line by fluorescent radiation of a wavelength just shorter than the edge for the element being determined. In the case of uranium in steel alloys, the principal effect is one of absorption; hence, standards having approximately the same composition as the samples are required. Alternatively, an internal standard can be used. However, choice of a suitable internal standard is a relatively complex matter, which also depends on the composition of the sample, since an element must be chosen having an analytical line which is affected by the sample conditions in the same way as the element being determined.

Many of the above difficulties are greatly reduced by mixing the sample with a suitable diluent. In the procedure described below, alumina is used for this purpose.

The chemical form of the sample can be of importance(139). For example, it is impossible to compare iron results between Fe, FeO, Fe_2O_3 and Fe_3O_4 by x-ray spectroscopy since, when the K_α line is used, oxygen is completely transparent to both the exciting and fluorescent x-radiation. As a result, the relative intensity of the iron K_α line will be almost identical in all cases. The physical state is even more critical(140). The sample surface presented to the instrument must be flat, uniform and reproducible. The necessity for this arises chiefly from the possibility that fluorescent radiation from material in crevices will be lost by absorption in traversing the sample material. For this reason, pellets pressed from metal chips or turnings do not make a very satisfactory form for direct x-ray analysis. They can be used, however, by a technique employing scattered target radiation as an internal standard(141). Cast discs machined flat make excellent specimens, and a chemical analysis performed on drillings from the back, or on millings from the analytical surface, permits the establishment of the composition of standards. Alternatively, the sample can be finely pulverized with an abrasive diluent in a high speed mixer-mill. The latter procedure, using alumina as the abrasive diluent, is described in Part III of this report; typical results are shown in Table 2, below:

TABLE 2

Typical Results of Uranium Analyses by X-ray Fluorescence Spectrometry Using the Alumina-Dilution Technique

Sample No.	Fluorimetric Value (%)	X-ray Value (%)
3673	0.57	0.58
3674	0.002	0.002
3675	0.36	0.36
3676	0.59	0.57
3677	0.81	0.85

8. Radiometric Methods

The usual radiometric procedures employed for the determination of uranium in ores depend on the presence of highly radioactive daughter elements which are formed over the course of eons. These daughters are eliminated in the refining process, so that the relatively pure uranium used in alloying is only weakly radioactive. Nevertheless, with suitable equipment and techniques, capable of measuring the low-energy radiation from the uranium and its immediate short-lived decay products, sufficient sensitivity can be obtained to determine the uranium content of the steel or alloy(142). The technique is a comparative one, making use of known samples calibrated by chemical assays; accurate calculation of the percent uranium in the unknown samples is then possible, provided the samples have been prepared within certain limits of size and density. Counting may be done using either of two methods: (1) by recording the rate at which beta particles are given off from the surface of a sample, or (2) by measuring the soft gamma-radiations emitted from a thin sample. The beta-ray method is simpler but, because it makes use of a surface effect, may be subject to serious error in case of non-uniform distribution of the uranium throughout the steel; special sample preparation can largely overcome this problem. The gamma-ray method, although requiring somewhat more complex equipment, provides greater accuracy. Both methods have about the same sensitivity.

The Beta-ray Counting Method

The beta-ray method is particularly useful for scanning the surface of a large sample to locate areas of high uranium concentration. A beta-sensitive Geiger tube with a sensitive area of at least one square inch is used in a probe, together with a ratemeter to give an immediate reading, or with a counter and recorder for a numerical indication. For example, a Victoreen No. 1B85 Geiger tube has been used with its axis parallel to the sample. Little shielding is required; thus the probe is light and easy to handle. The effect is a surface one, so that there is very little interference from radioactive materials within the sample.

The fact that this is a measurement of surface activity may cause serious error in some instances if the results are considered representative for the whole sample volume. If small (10-20 grams) samples are to be counted below a Geiger tube, the sample should be mixed mechanically to increase the uniformity with which the uranium is distributed in the steel sample. About 20 grams of fine steel drillings or turnings are spread out in a tray (aluminum pie plates can be used) and sprayed with a very thin coating of a plastic lacquer (Hughes-Owens "Crystal Clear", No. A-1159), which is then allowed to dry. The coated filings are pressed in a cylindrical mould 1.25 inches in diameter at room temperature using a pressure of 20,000 psi to produce a pellet approx. 3/16 inch thick. A few such pellets were counted beneath an Anton No. 1001H mica-window Geiger tube mounted in a lead shield whose walls were 2 inches thick. Under these conditions the background was equal to that from a sample containing 0.008% U. The calculated percentages of uranium agreed reasonably well with those obtained for the same sample by the gamma-ray method. Values from both methods are given later (Table 3, page 46). Additional care in regard to uniformity of surface texture should be taken if the accuracy of this method is to be improved. A two-inch mould could be used to double the surface area, and therefore the sensitivity (uranium equivalent of background reading).

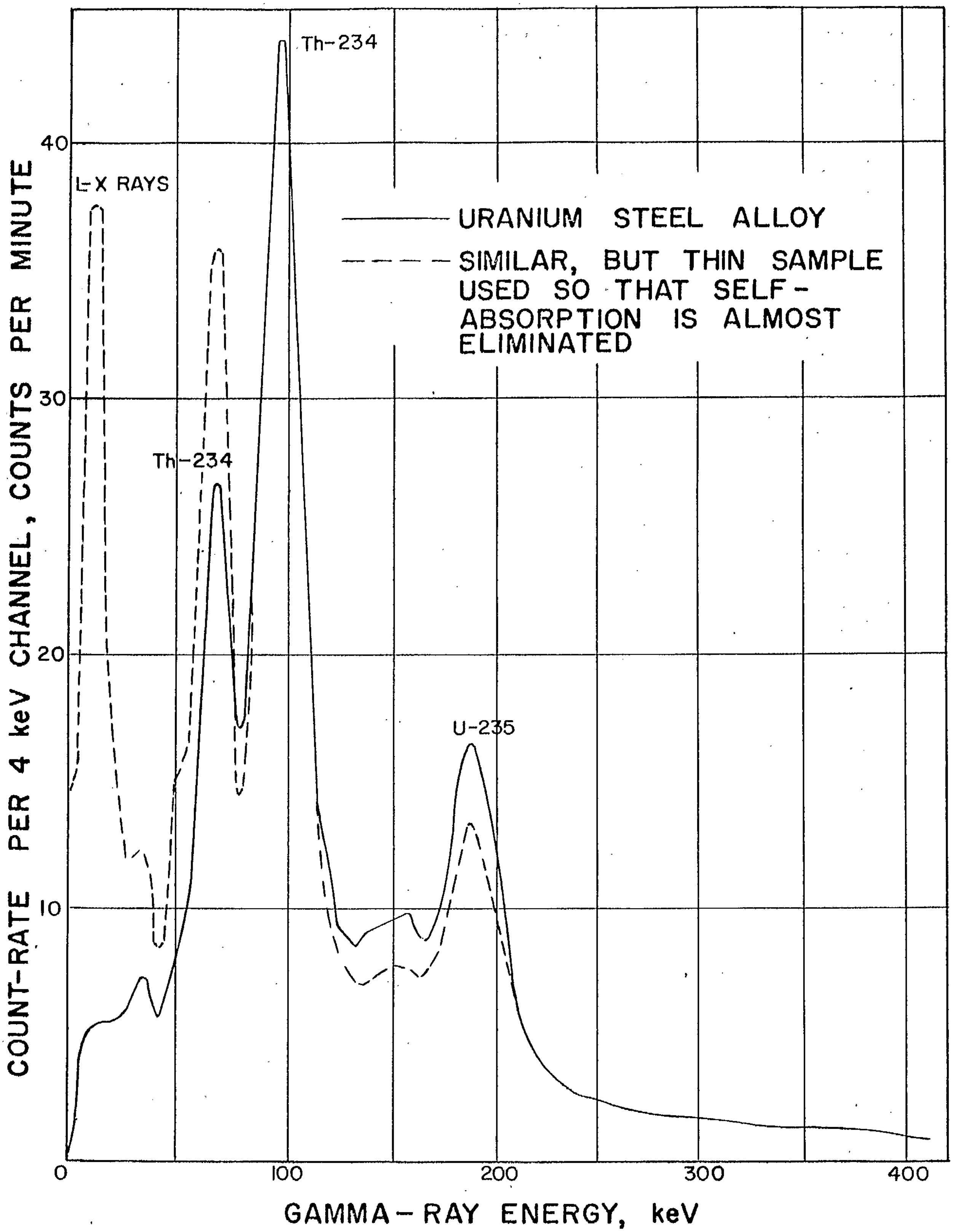
The Gamma-ray Counting Method

In this method a scintillation counter is used whose detecting crystal is 2 inches in diameter and 1/2 inch thick. The detector is surrounded by a lead shield 2 inches thick. To gain the most favourable response relative to background radiation, counting is restricted to an energy interval from 60 to about 200 keV. The interval is not critical, but for good counting statistics, the expression $\frac{S^2}{B}$ (where S is the count rate from a sample and B is the background count for the same energy range) should approach a maximum.

A single-channel pulse analyzer and counter is, therefore, used (e.g., Nuclear-Chicago Corporation No. 132B) instead of an ordinary scaler, so that background counts above 200 keV can be rejected. Another advantage of this instrument is that it includes a preamplifier. The photomultiplier tube used is an R.C.A. type 6655, a tube found to be less affected by change-in-gain with change-in-count-rate than some other types. The principal gamma-ray emitter is 24-day thorium-234 (UX_1) with a prominent line at 91 keV, with a lesser contribution from other immediate decay products of uranium-238. The isotope uranium-235 makes a measurable contribution; therefore, if depleted uranium is used in alloy work, similar standard samples would be required to prevent a small error on this account. No correction need be made for the build-up of Pa-234 (UX_2) to equilibrium with its parent after purification, provided (as will generally be the case) the uranium is more than a few months old, or provided that the standard calibration samples are prepared from the same batch of uranium. The gamma-rays occurring in the previously-stated energy interval are relatively soft, so that internal absorption within the sample becomes a problem; therefore, sample thickness should preferably be limited to about 0.25 inch for solid or compressed material. Figure 4 shows a gamma-ray spectrogram of a typical uranium-bearing steel alloy.

Uranium steel samples have been counted in several forms: thin solid bars; coarse and fine fragmented material, such as filings or drillings; and compressed fragments bound together by a thin coating of a plastic binder. The mass of the sample should be about 10 to 40 grams.

Loose fragments of metal may be counted if required, but there will be difficulty in achieving accuracy if long drillings are used



Uranium-Steel Alloy, 20 grams - 0.58% U.

Figure 4. Gamma-ray spectrogram of a typical uranium-bearing steel alloy.

which preclude a definite estimate of the sample thickness. For this reason a drill bit should be used which has been ground to produce fine drillings, thereby improving compaction and sample uniformity.

It is better to use solid samples or compressed samples of uniform size and weight. (The procedure for preparing 20-gram pellets has been outlined already in the section on the beta method.) If the weight must vary, an empirical weight correction curve is easily produced. Both sides of the pellet can be counted to provide increased accuracy.

A counting period of five minutes or less for each face of a pellet will usually suffice; during this interval there will be enough time to prepare another sample. Typical results from both the beta and gamma methods are shown in Table 3.

The counting intervals shown can also be chosen, by means of a standard sample, to read "per cent uranium" directly. This value would include the background which can be thought of as "equivalent per cent U" and subtracted from the direct reading. For a typical sample* this would appear as follows: (Both sides of the pellet are counted.)

No. 1721	gamma	(0.056-0.011)%,	side No. 1	0.049% U (mean)
		(0.065-0.011)%,	side No. 2	
No. 1721	beta	(0.050-0.0081)%,	side No. 1	0.042% U (mean)
		(0.050-0.0081)%,	side No. 2	

---

*These values are based on a 20-gram pellet, 1.25 inches in diameter, and sensitivities of (1) gamma, 3000 counts/min/1% U, and (2) beta, 2400 counts/min/1% U.

TABLE 3

Typical Results of Uranium Analyses by the Radiometric Method

Sample No.	Net count/min, gamma method		Net count/min, beta method		Per cent Uranium	
	Side No. 1*	Side No. 2*	Side No. 1*	Side No. 2*	Gamma	Fluorimetric
	**					
1719	36 (3)	33	19.6 (5)	11.2	0.012	0.010
1720	53 (3)	45			0.016	0.016
1721	140 (3)	165	121 (5)	120	0.050	0.051
1722	150 (3)	147			0.049	0.060
1723	382 (3)	380			0.13	0.14
1724	1067 (3)	1041	785 (5)	817	0.35	0.39
1725	2378 (1)	2441			0.79	0.98
1726	4771 (1)	4675			1.56	1.64
1727	6021 (1)	5944	5190 (1)	5337	1.97	1.69
1728	4335 (1)	4318			1.43	1.41
Background	33/min (gamma)		19.4/min (beta)			

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[*] Both sides of the pellet are counted.

[**] Numbers in brackets indicate actual counting interval per side.

PART III. TYPICAL ANALYTICAL PROCEDURES

The chemical methods described here have been purposely selected to illustrate those methods for the separation and determination of uranium that are believed to be most generally applicable in steel analysis. In the case of a specific mixture of alloying constituents, different combinations of the steps may be possible, due to the absence of a particular set of interfering elements, with a resulting simplification of the method. Alternatively, a study of the discussion in Parts I and II, in the light of the known composition of the alloy, may permit the choice of a combination of methods, for the separation and determination of the uranium, which is simpler than any of those described below.

A. VOLUMETRIC METHOD

Outline

This method employs a cupferron separation from sulphuric acid solution to effect the separation of iron and uranium. Following the separation, the uranium is reduced by titanous sulphate solution and the uranous ion is titrated with a standard solution of potassium dichromate.

Since, in addition to the iron, the cupferron extraction removes vanadium, titanium, molybdenum and tin, the procedure will be useful for master alloys containing these elements. Zirconium, niobium and tungsten are also precipitated by cupferron (somewhat higher acidity than is recommended here is necessary to effect complete separation of the tungsten precipitate), but the precipitates in this case are soluble only with difficulty in chloroform. Hence, if these elements are present in quantity, it will be necessary to filter off the cupferron precipitate rather than extract it. The filtration should be carried out rapidly, using very cold solutions to avoid decomposition of the reagent.

The method described for dissolving the sample is satisfactory for use with the ferro-alloy, but would have to be modified for master alloys containing large amounts of refractory metals.

For example, uranium-titanium alloys are attacked only slowly by this procedure, but respond well to the treatments usually employed to dissolve titanium metal. With unusual master alloys, it is necessary to use caution in establishing a suitable dissolution procedure. Zirconium alloys in particular are said to react vigorously under oxidizing conditions, and the use of nitric acid must be avoided in dissolving zirconium-uranium mixtures. Many finely divided metals tend to react rather violently with acids and oxidants, so that samples in the form of powders will also require cautious treatment.

Range

The method as written is designed to be suitable for alloys containing more than 25% uranium. If the uranium content is lower than this, a larger sample should be taken and the bulk of the iron eliminated by a mercury cathode separation, details of which are included in Part III, under "C. Colorimetric Method" (pages 78-82).

Apparatus

Erlenmeyer flasks, Pyrex narrow-mouth:	500-ml size
Separatory funnels, Squibb pear shaped:	300-ml size
Cooling bath, 5°C:	Approx 14"x28"x12" deep
Volumetric flasks:	100-ml size
Pipettes:	25-ml size
Burette:	50-ml size

Reagents

Nitric acid, conc:

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

Sulphuric acid, conc:

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

Hydrochloric acid, conc:

Hydrofluoric acid:

Hydrogen peroxide, 30%:

Cupferron solution, 8%: Dissolve 40 grams of cupferron in water, dilute to 500 ml and filter if necessary. Store in a dark bottle in a refrigerator and cool to 5°C before use. Prepare fresh weekly.

(Reagents, cont'd)

Chloroform:	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%:	
Titanous sulphate solution, 10%:	Measure 200 ml of 15% (v / v) sulphuric acid into a 400-ml beaker. Bring to a boil and add 5 grams of titanium hydride in 0.5-gram portions over a period of 1/2 hour. Once every 10 minutes, remove the beaker from the hot plate, and add boiling water to bring the volume back to 200 ml. When the titanium hydride is completely dissolved, let the solution cool, decant into a clear bottle, and close with a vented stopper. The solution may be used as long as not more than 5 ml are required to reduce 150 mg of uranium.
Mercuric perchlorate solution, 8%:	Dissolve in water, adding a few drops of perchloric acid to ensure complete solution.
Ferric sulphate solution, 20%:	Dissolve 200 grams 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 orthophosphoric acid (85%) with 26 ml of concentrated sulphuric acid.

(Reagents, concluded)

Ferric sulphate solution, 20%:	Dissolve 200 grams 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 orthophosphoric acid (85%) with 26 ml of concentrated sulphuric acid.
Sodium diphenylamine sulphonate solution:	
Potassium dichromate solution (0.025N):	Prepare from the primary standard salt or standardize against iron wire.

Procedure

Sample Solution

Weigh a 1-gram sample into a 250-ml beaker. Add 25 ml of aqua regia (cautiously), cover the beaker, and let stand in the cold till the reaction subsides. Remove the cover, add 15-20 ml of dilute (1:1, v/v) sulphuric acid, and evaporate just to strong fumes. Cool, cautiously add 50 ml water, and warm to dissolve. If necessary, add a few drops of 30% hydrogen peroxide. Transfer to a 100-ml volumetric flask, and dilute to the mark with water.

Cupferron Extraction

Pipette a 25-ml aliquot into a 300-ml separatory funnel. Add sufficient dilute (1:1, v/v) sulphuric acid so that the total content is equivalent to 10 ml of concentrated acid. Dilute to 100 ml, add dilute potassium permanganate solution until a faint pink colour persists, 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 solution, 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.

After completion of the final chloroform extraction, wash the sample solution into a 300-ml Erlenmeyer flask. Add glass beads and evaporate to about 35 ml. Add 35 ml of nitric acid and evaporate to fumes of sulphuric acid. 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. Repeat the steps of this paragraph until all organic matter is removed.

Reduction and Titration

Carry a reagent blank through this part of the procedure. 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 hydrogen peroxide. Boil to dissolve. Cool and add 2 ml of 5% copper sulphate solution. Add titanous sulphate solution by means of a 10-ml burette until a faint permanent darkening of the solution takes place due to precipitation of metallic copper. Add an excess of the titanous sulphate solution of about 20% of the initial volume added (e.g., if 2 ml are required, add 0.4 ml excess). Swirl the solution continuously during this step. (If more than 5 ml of the titanous sulphate solution is required, the solution is exhausted and should be discarded.)

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. 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 where 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 steps, is subtracted from the titrations of samples and standards. The net titration is recorded.

Calculation

I ml 0.025N potassium dichromate solution ≈ 0.002975 g U.

B. FLUORIMETRIC METHOD

Outline

This method is based on the measurement of the fluorescence produced when uranium, fused into beads of sodium fluoride, is illuminated with ultra-violet light. Large amounts of certain elements, such as iron, tend to decrease the fluorescent output, and in the following procedure, ethyl acetate extraction of uranyl nitrate from an aluminum nitrate medium is used to effect a separation of uranium from iron. This extraction separation procedure eliminates virtually all other elements, although a small fraction of any zirconium, titanium or thorium present will probably accompany the uranium.

Range

The method as written will permit the determination of as little as 0.001% uranium. It can be used to analyze almost any uranium-bearing alloy, but for precise results in the higher ranges a colorimetric or volumetric method is preferable.

Apparatus

Separatory funnels:	Pyrex, Squibb pear-shaped, 60-ml, Teflon stopcocks.
Stoppers, polyethylene:	To fit funnels.
Buchner funnel:	Size No. 2.
Flask, filtering:	250 ml size.
Flasks, volumetric:	25, 50, 100, 250, 500 ml sizes.

Apparatus, (cont'd)

Pipettes, volumetric:	5, 10 ml sizes.
Micropipettes:	100λ, similar to Microchemical Specialties Co. Catalogue No. 282a.
Platinum dishes:	Pressed from 3/4" x 0.015" platinum-rhodium alloy (see Figure 5). Used in sets of 22.
Trays for platinum dishes:	A separate tray is used for each set of dishes. See Figure 6.
Platinum-tipped forceps:	
Infra-red drying apparatus:	An enclosed transite box containing four 100-watt infrared lamps, controlled by a 2 KVA Powerstat.
Apparatus for storing salting solution:	See Figure 7.

Reaction kettle, 3-neck:	Similar to Ace 6476, 6486, all 3 joints 24/40.
Condenser, water-cooled:	With 24/40 joints.
Thermometer well:	Ace 5295 J. 24/40.
Thermometer:	0-150°C.
Glass stopper:	24/40.
Heating mantle:	Similar to Ace 6478.
Variac control:	0-135 volts, 7.5 amp.

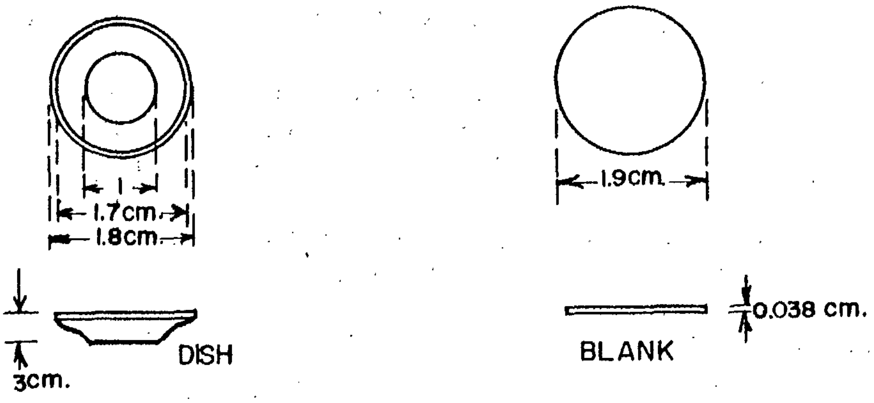

Figure 5. Details of platinum dish for fluoride bead.

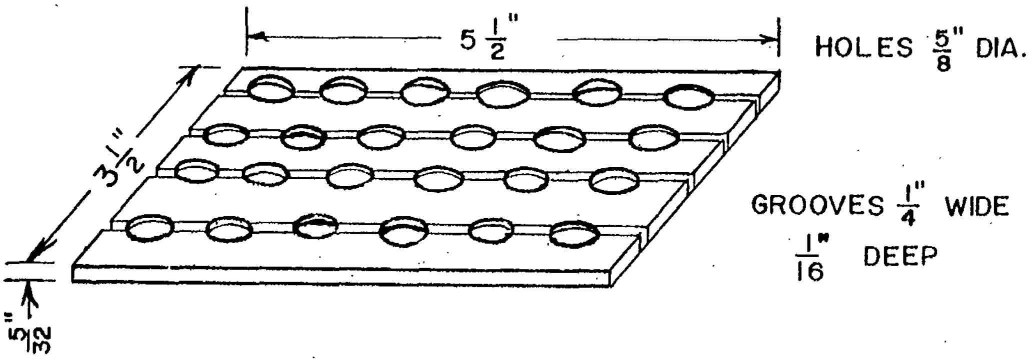

Figure 6. Tray for platinum dishes.

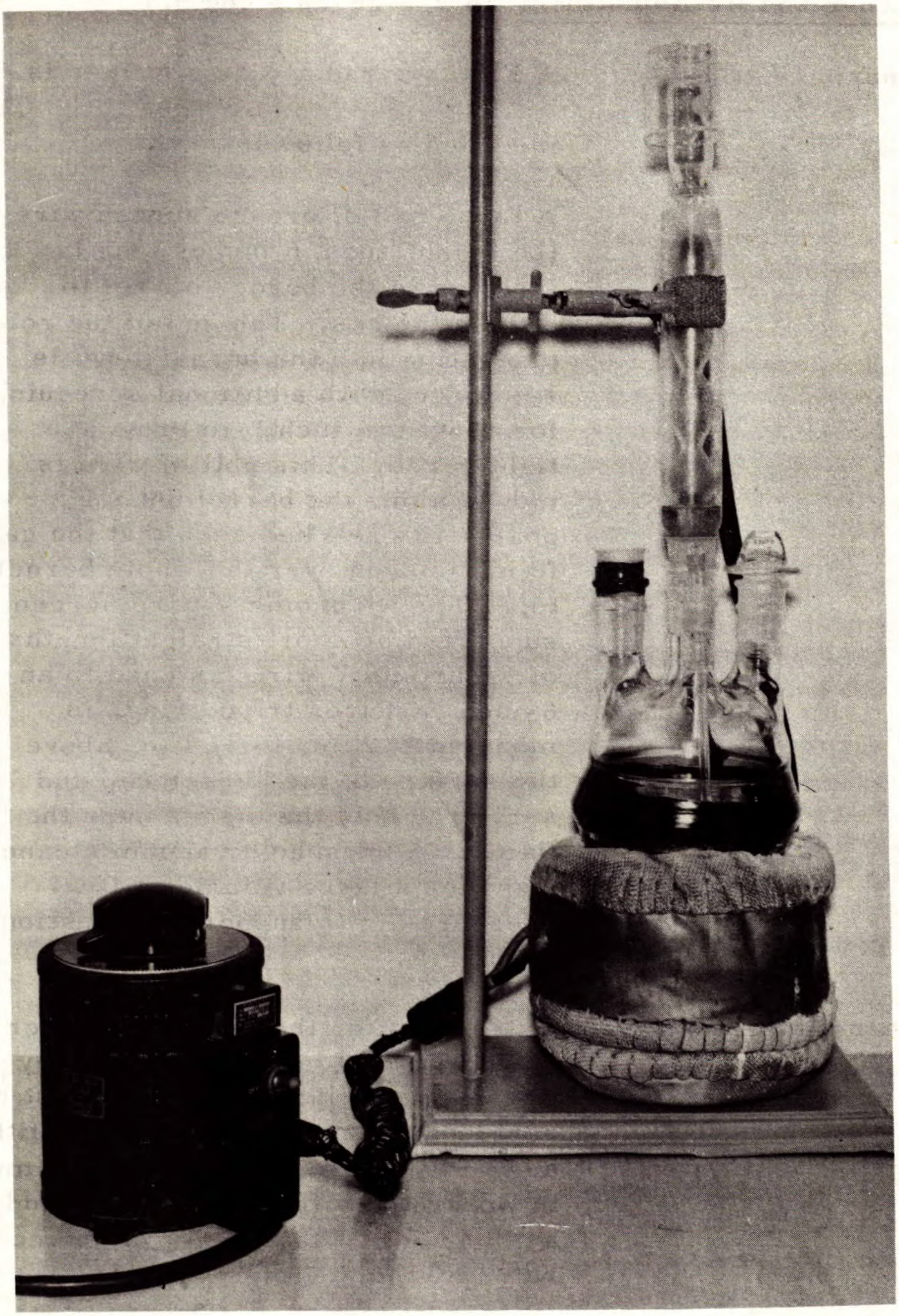

Figure 7. Aluminum nitrate storage container.

The Gas Burner and its Adjustment (See Figures 8 and 9.)

Gas Burner:	A Fletcher radial-flame burner is modified as follows: 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 1/2 in. to 3/4 in. above the surface of the burner cap and serves to hold the dishes over the flame. A household vacuum cleaner provides a large volume of low-pressure air to support combustion of the gas.
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 from leaking around it and burning at the edge, which accelerates warping.
Nichrome Wire Screens:	Circles of 5-mesh, 16-gauge Nichrome V wire screens, 4 1/2 in. 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

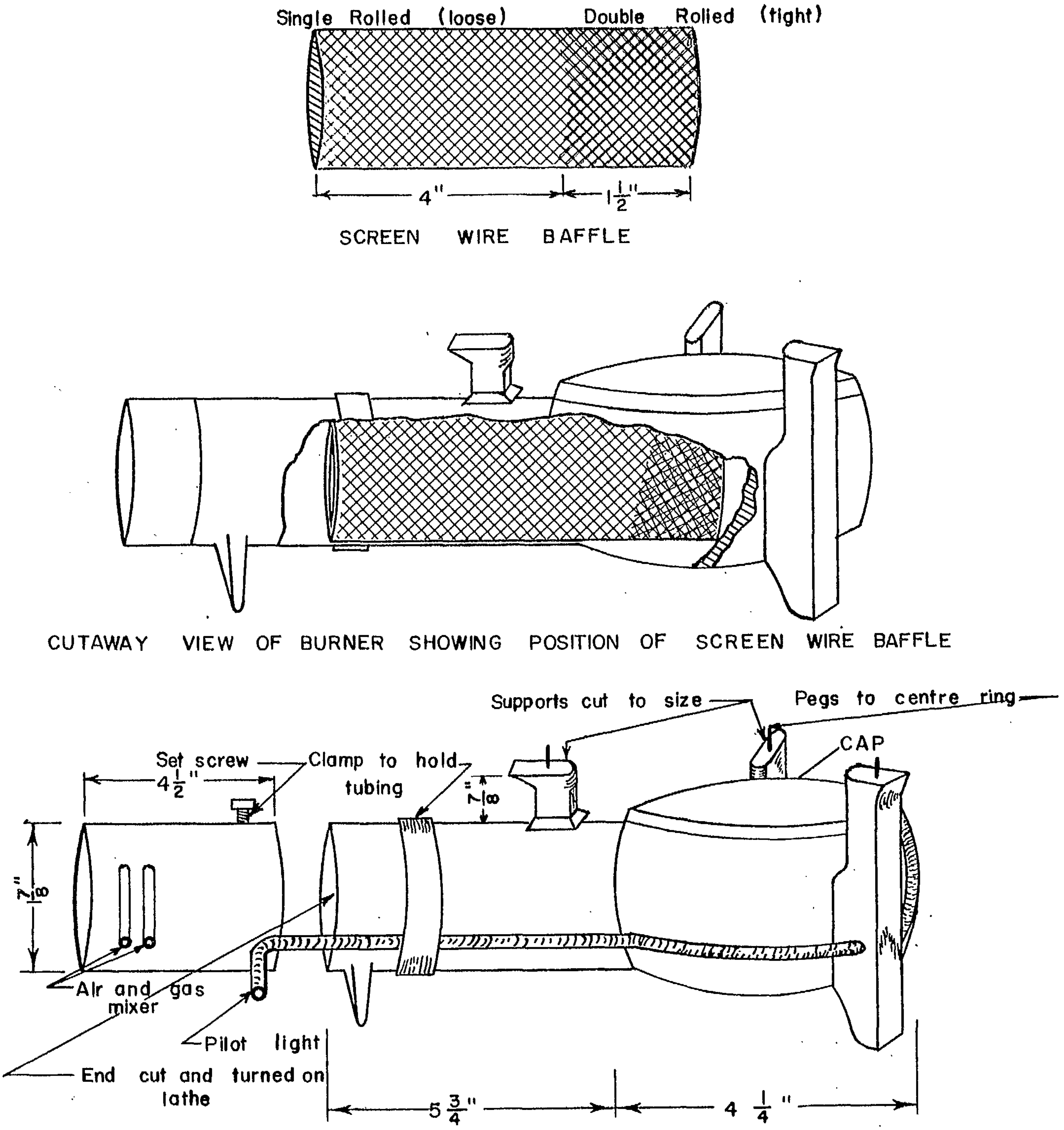

Figure 8. Details of modified Fletcher radial-flame burner (compressed air supply).

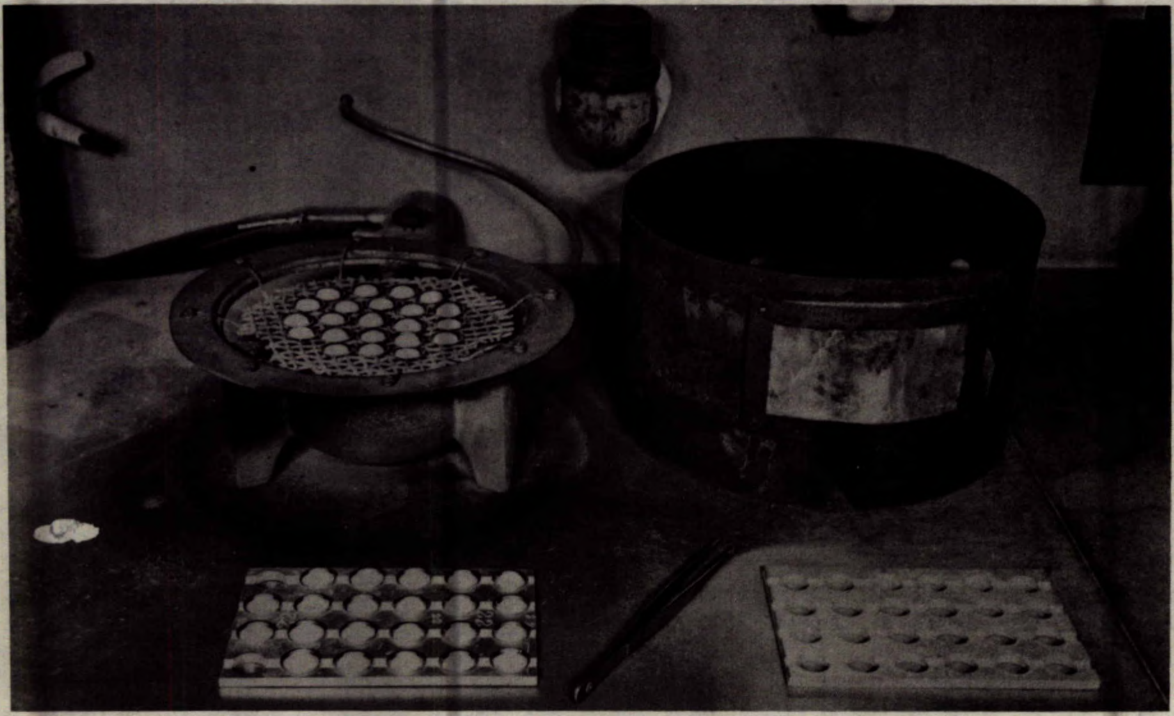

Figure 9. Gas burner, dishes, and trays.

gas cones are 1/4 in. to 3/8 in. 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, by means of an adjustable air escape port, until the burner "howls". Cut the air back just sufficiently to prevent the howling, and leave the air setting in this position. Note the gas flow setting and then shut off the burner.

Measure a flux pellet 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 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 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 with the gas. It appears desirable to use a flame which is just hot enough to melt the pellet in the 1 1/2 minute period. Too rapidly melting leads to quenching. On the other hand, too slow a fusion wastes gas and may result in quenching.

Fume Hood: (Figure 10)

A standard commercial 4 foot hood, lined with firebrick (and fitted with a suitable flame baffle consisting of 2 sheets of heavy 1/4 in. mesh wire screening in the upper portion to protect the exhaust fan) is required

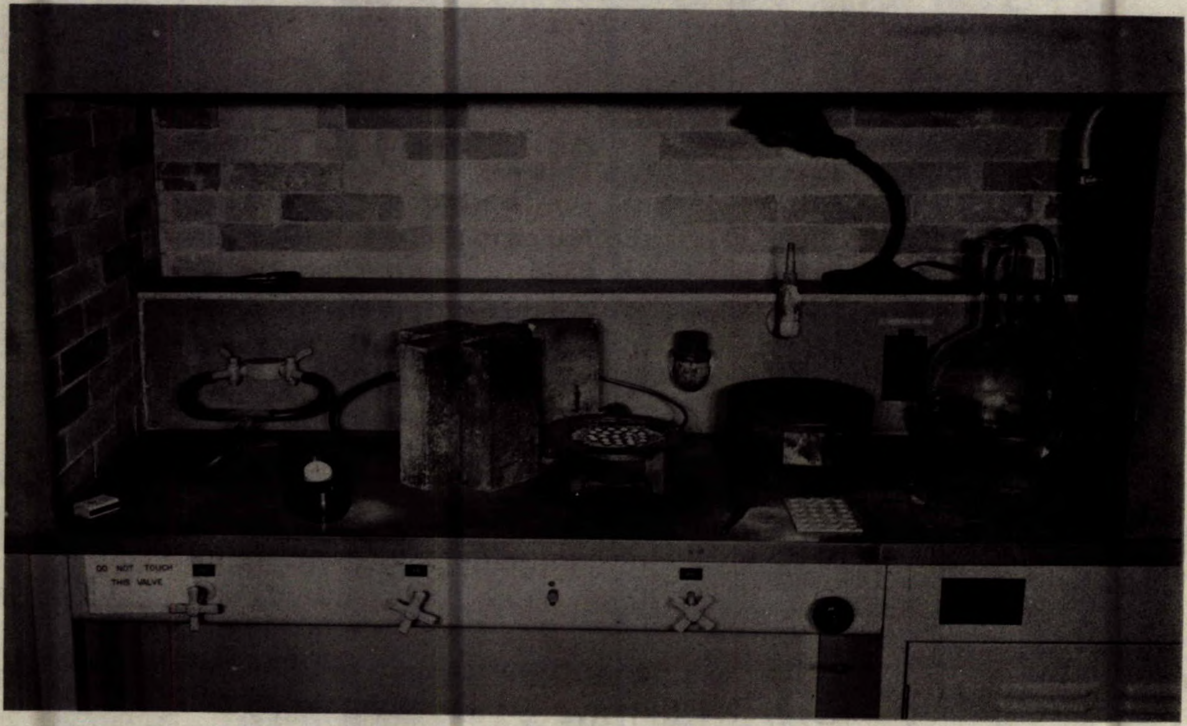

Figure 10. Fume hood.

to house the gas burner. 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 1/4 in. asbestos board, with an 8 in. x 8 in. mica window to shield the operator while providing for observation of the flame, is used.

Galvanek-Morrison Fluorimeter: (Figure 11)

This is the most commonly used commercial fluorimeter. It is illustrated in Figure 11, together with its power supply.

The ultra-violet source consists of two 4-watt, fluorescent-type ultraviolet 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. It consists of an RCA 1 P 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 read on 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

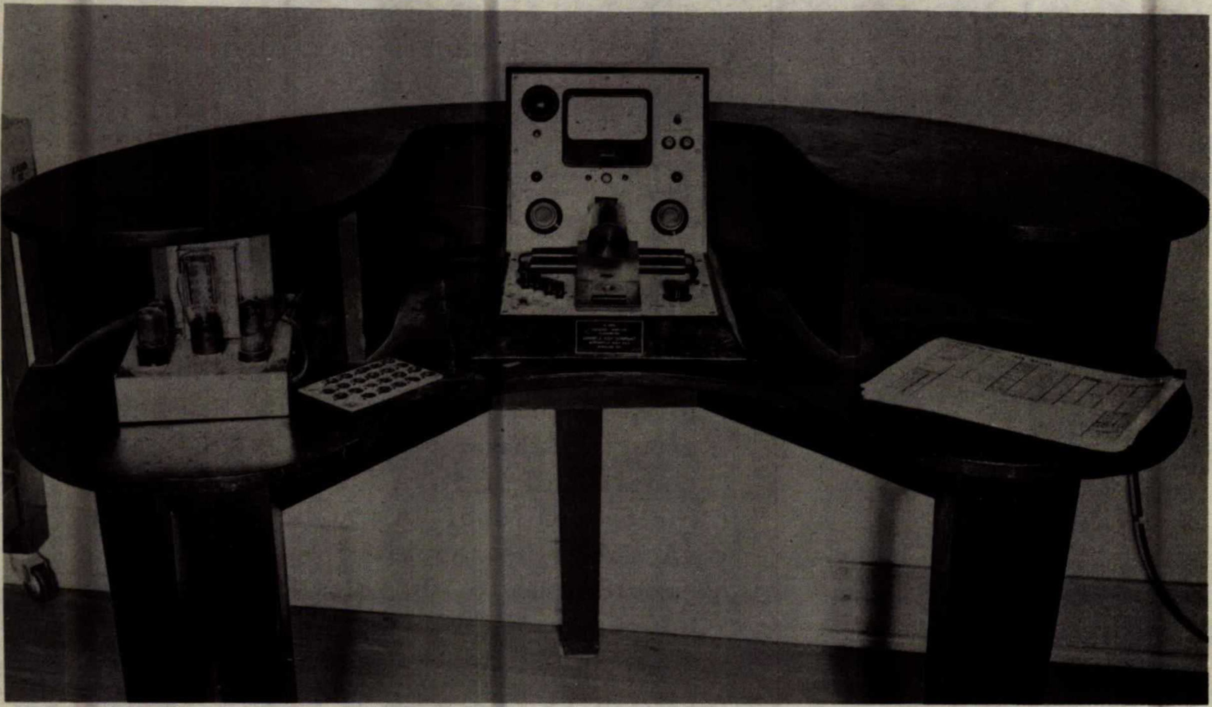

Figure 11. Fluorimeter.

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. It is provided with a series of range switches in keyboard arrangement. When the sample is introduced into the light chamber, the meter is automatically set to its highest range, providing protection for the microammeter. In reading the fluorescence, the range switches are actuated in order from right to left till the highest value that is still on scale is obtained. 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.

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 on the front of the power supply. 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.

Checking Linearity of Instrument Response

With a new instrument it is good practice to verify that it 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 x galvanometer response against uranium concentration. 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 whether this will improve performance.

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, one sample with each of ten fusions. Calculate the standard deviation and absolute error.

Cleaning the Platinum Dishes

Wash the dishes in running hot water for 1/2 hour. 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 with concentrated hydrochloric acid and boil them for 1/2 hour. Pour off the acid and rinse well with tap water. Repeat the acid treatment and the 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 adsorbed into the dishes. From time to time the dishes may also be cleaned with molten potassium bisulphate in a Vycor dish. Eventually the dishes absorb so much iron and other quenchers that erratic results are obtained. About once a year, depending on use, the used platinum dishes should be exchanged for new ones.

Reagents

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

Nitric acid, CP

Nitric acid, 5% v/v (50 ml per litre)

Hydrochloric acid, CP

Hydrochloric acid, 16% v/v

Ethyl acetate, reagent grade

Aluminum nitrate, CP:	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 pound.

Aluminum nitrate salting solutions:	Place approximately 1800 grams (4 lb) of aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$) 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 the 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. Whatman No. 42 or equivalent, 7 cm circle.
Sodium carbonate:	Reagent grade.

Standard uranium solution:	Dissolve 0.118 g U_3O_8 in 100 ml 5% acid. Dilute 1 ml to 1000 ml with 5% nitric acid; 0.1 ml = 100 mγU.
Sodium fluoride--lithium fluoride pellets (98:2), 0.600 g:	These pellets are obtainable commercially. They should be tested for fluorescence under normal fusing conditions, with or without standard uranium addition. With the 100 milligamma U_3O_8 standard aliquot, they should give a meter reading of 500 units with the Galvanek-Morrison instrument, and blanks of 10 to 20 units.

Procedure

Plain Carbon Steel

Weigh a 2-gram sample into a 250-ml beaker. Add 25 ml concentrated nitric acid, 15 to 20 ml of water, and slowly add concentrated hydrochloric acid dropwise until the steel begins to react (only a few drops are needed). When the initial reaction subsides, cover the beaker with a watch-glass, transfer to a hot plate, and boil until the sample is completely dissolved. Usually there is no residue but if any is found, treat it by the fusion procedure described under "Stainless Steel", below. Combine the solution from the fusion with the main solution, transfer to a 250-ml volumetric flask, and dilute to the mark with 5% nitric acid. Proceed to the ethyl acetate extraction next.

Stainless Steel

Weigh a 2-gram sample into a 250-ml beaker. Add 25 ml concentrated nitric acid, 15 to 20 ml water, and stir. Slowly add concentrated hydrochloric acid until the sample starts to dissolve (about 10 to 40 ml will be required). Cover with a watch glass and, when the initial reaction subsides, transfer to a hot plate and boil until decomposition is complete. Filter the hot solution with suction, using a No. 2 Buchner funnel and a 7-cm No. 42 Whatman filter paper. Wash the residue on the paper thoroughly with hot water. Transfer the filtrate in the suction flask to a 250-ml volumetric flask, completing the transfer with water. Reserve this solution. Place the paper in a 40-ml platinum crucible, dry, and ignite at low heat. Add 2 to 3 grams of potassium pyrosulphate and fuse at 700-800°C. Cool and dissolve the melt in 5% (v/v) nitric acid, adding the solution to the volumetric flask containing the main solution. Dilute to the mark with 5% (v/v) nitric acid. Proceed to the ethyl acetate extraction next.

High Speed Steel

Weigh a 1- or 2-gram sample into a 250-ml beaker, and add 25 ml of aqua regia. Cover with a watch glass, transfer to a hot plate, and bring to a boil. When the sample is completely decomposed, filter as before and wash with hot water. Transfer the filtrate and washings to a volumetric flask of suitable size, and dilute to the mark with 5% nitric acid. In general, uranium is not occluded by any hydrolytic precipitate that deposits out, but may be contained in any undissolved residues. Proceed to the ethyl acetate extraction next.

"Acid Insoluble" Uranium:
(Uranium insoluble in 16% v/v hydrochloric acid)

Weigh a 2-gram sample into a 250-ml beaker. Add 50 ml water and 8 ml concentrated hydrochloric acid. Place the beaker on an asbestos-padded hot plate and warm. Do not boil or agitate. Let the sample digest on the warm hot plate until nothing remains that is attracted by a hand-magnet held under the beaker.*

Filter the sample, wash the residue with warm water, and discard the filtrate and washings. Place the filter paper, containing the undissolved residue, in the original beaker. Return the beaker to the hot plate, let it dry well, and ignite it so as to burn off the paper as completely as possible. Treat any residual carbon in the beaker with concentrated sulphuric and nitric acids until completely destroyed and fume to dryness. Transfer the contents of the beaker to a volumetric flask of suitable size and make to volume with 5% (v/v) nitric acid. Filter a portion of the solution from the volumetric flask. Normally, the ethyl acetate separation can be omitted. Carry out a second dilution, if necessary, and proceed to the paragraph headed "Aliquoting the Samples into the Platinum Dishes" (page 73).

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*Note: Plain carbon steels will dissolve in about 1/2 hour. High alloy steels often require several days' treatment, with additions of 16% acid as make-up. Many high-alloy steels are not attracted by a magnet and dissolution must be followed visually.

Ethyl Acetate Extraction

Pipette a suitable aliquot of the sample solution (see Table 4) into a 60-ml separatory funnel. Add, by means of a graduated pipette, 6.5 ml of aluminum nitrate solution (at 110°C) for every 5 ml of sample solution taken. Cool the solution to room temperature and add 20 ml of ethyl acetate. Stopper the separatory funnel with a polyethylene stopper and shake the funnel for 45-60 seconds. If crystallization takes place near the stopcock, place the lower part of the funnel in a beaker of hot water until the solidified material redissolves.

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

TABLE 4

Sample Size and Dilution

Range, % U	Solution		Extraction	
	Sample size, grams	Dilute to ml	Take ml	Dilute to ml
< 0.01	2	50	10	25
0.01 - 0.10	2	100	10	50
0.10 - 0.50	2	250	5	100
0.50 - 1.0	2	500	5	250
> 1.0	Dilute proportionately.			

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 (into the funnel) with a jet from a wash bottle, drain the aqueous layer into a volumetric flask of suitable size (Table 4). Wash the separatory funnel and the ethyl acetate layer four or five times with 5-ml portions of water, and add the washings to the volumetric flask. Make the solution in the flask to volume with 5% nitric acid.

Aliquoting the Samples into the Platinum Dishes

Lay out the set of clean dishes (22 in all) on the tray (Figure 12), using platinum-tipped forceps. Place the tray in the infra-red drier for several minutes. Remove the tray of dishes from the drier and let it cool. Pipette the samples into the dry dishes with a 100-λ micropipette held in a rubber bulb, using one set of dishes for every two samples. In preparing the dishes, rinse the pipette with the first sample and pipette an aliquot into each of 5 dishes. Rinse the pipette with the second sample, and pipette an aliquot into each of the next 5 dishes. Finally, rinse the pipette with the standard uranium solution ($100\lambda = 100$ mγ U) and pipette an aliquot into the next 10 dishes. Leave two dishes empty, as blanks.

Return the tray of dishes, containing the aliquots of standard and sample solutions, to the infra-red drying oven and let them dry slowly so they do not spit.

Remove the tray of dry dishes and place a pellet of the flux in each dish.

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 13.

The Fusion

Turn on the gas supply to the Fletcher burner and ignite it. Adjust the gas flow to a value that has been found to give satisfactory fusing conditions (see the section, "The Gas Burner and Its Adjustment", page 58).

Turn on the air supply and adjust the gas control 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 1 1/2 minutes. The melting time is checked by means of a stopwatch. When the fusion is complete, shut off the gas and air and play a stream of steam over the burner and beads until they 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.

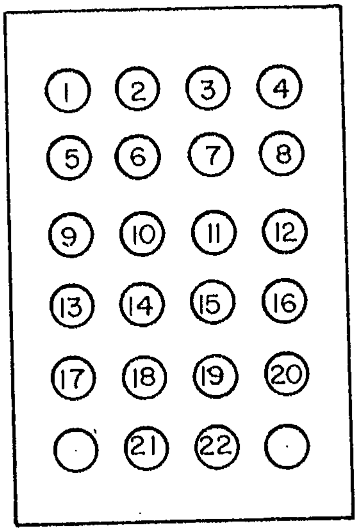

Figure 12. Order of dishes in tray.

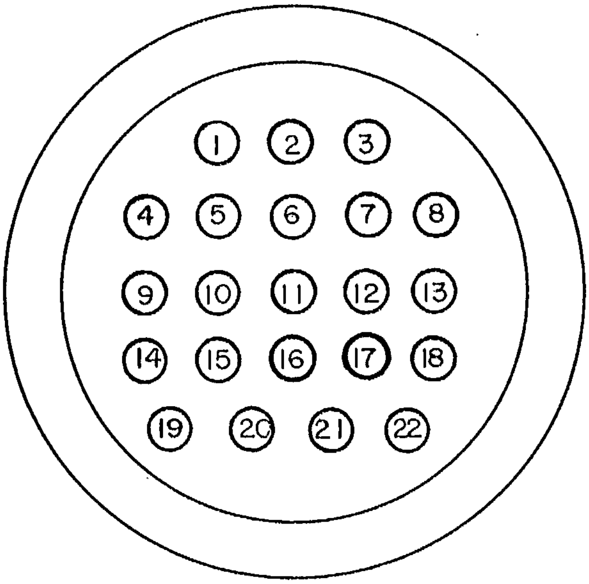

Figure 13. Order of laying out dishes on burner.

Fluorimeter Operation--GM Fluorimeter

The following revised procedure simplifies the reading of the fluorescence:

Remove the 100-mγ (white) standard from the standard position by lifting out the front stop, drawing out the sample slide, removing the standard, and replacing the slide as before. The former standard position (slide fully out) is now used for dark current adjustment.

Turn the instrument on and allow it to warm up for 15 minutes. Pull the slide out and insert one of the 100-mγ standard beads. With the slide out, zero the instrument by depressing the zero switch and adjusting the microammeter. (Alternatively, a quicker adjustment can be made by pushing the slide in and adjusting the microammeter without depressing the zero switch.) 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 voltages until the microammeter reads about 50 microamperes. Re-zero the instrument and repeat the adjustment. Now pull the slide out and adjust the dark current control so as to re-zero the instrument.

With the sample slide out, remove the standard bead and insert the sample bead (removed from its dish). Move the slide in, and close successive multiplier switches from right to left until the maximum reading that is still on scale is obtained. Note and record the reading. Release the multiplier switch (with the slide in) and note the zero reading.

Pull the slide out to remove the sample bead, and replace it with the next one. Continue reading the beads and checking the zero until all the beads are read.

Calculation

$$\% \text{ U} = \frac{\text{1st dilution aliquot (ml)}}{\text{sample wt}} \times \frac{\text{2nd dilution}}{\text{1st dilution aliquot}} \times \frac{\text{m}\gamma\text{ U in bead}^{*}}{\text{2nd dilution aliquot (ml)}} \times \frac{100}{10^9}.$$

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[*] Note: "mγ U 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.

C. COLORIMETRIC METHOD

Outline

This procedure employs, for the final determination step, the yellow colour of the complex formed between uranyl and thiocyanate ions in acid solutions. Some iron can be tolerated by reducing it with stannous chloride during the colour development, but the bulk of it must be removed and this is accomplished with the mercury cathode. The subsequent cupferron extraction step is necessary to remove molybdenum, titanium and vanadium, which also interfere. The cupferron treatment is also capable of removing iron, but in the case of a steel sample a rather large number of extractions is required, and a quick preliminary mercury cathode treatment will substantially shorten the overall time for the procedure.

It has already been noted (in "Volumetric Method", page 47) that the cupferrates of zirconium, niobium and tungsten are sparingly soluble in chloroform; hence, if these metals are major constituents of the alloy, the precipitate will have to be removed by filtration rather than by extraction.

Range

The mercury cathode-cupferron-thiocyanate colorimetric procedure described here covers the range 0.05% uranium and up. It is suggested for use in analyzing the occasional sample when fluorimetric facilities are not available. It is also suitable for determining uranium in the higher ranges and is faster than the volumetric method. The coefficient of variation is better than 1%, determined at the 2-mg level.

Apparatus

Mercury cathode, high current type:	Eberbach Dyna-Cath, or equivalent.
Separatory funnel:	125-ml size with Teflon stopcocks.
Flasks, volumetric:	100-ml size.
Spectrophotometer:	Beckman Model B or equivalent.
Spectrophotometer cells, Corex:	1-cm and 5-cm path length.

Reagents

Sulphuric acid, dilute:	1:1 v/v 10% v/v 2% v/v
Hydrochloric acid:	
Hydrochloric acid, dilute:	10% v/v
Nitric acid:	
Ammonium hydroxide (carbonate free):	
Potassium pyrosulphate:	
Aluminum chloride solution:	1 ml = 1 mg Al
Ammonium chloride:	
Ammonium chloride solution, 2%:	
Potassium permanganate, saturated solution:	

Cupferron solution, 8% aqueous:	Store in a refrigerator. Prepare fresh weekly.
Chloroform:	
Stannous chloride solution, 10%:	
Ammonium thiocyanate solution, 50%:	

Procedure

Weigh 2 grams of sample into a 400-ml beaker. Add 25 ml of 10% v/v sulphuric acid, cover with a watch glass, and heat to dissolve. If necessary, add hydrochloric or nitric acid to complete solution of the sample. When solution is complete, evaporate to strong fumes. If nitric or hydrochloric acid was used, wash down the sides of the beaker and fume again. Cool, take up in 50 ml of water, and warm to dissolve the salts. Filter if necessary, and wash the paper with a little 2% v/v sulphuric acid. If the residue contains uranium, transfer the paper to a platinum crucible, dry, and burn off at a low temperature. Fuse with 2 or 3 grams of potassium pyrosulphate. Cool and dissolve the melt, and combine with the main portion of the solution.

Mercury Cathode Separation

To the combined solution add ammonia dropwise until the solution becomes slightly turbid. Add dilute sulphuric acid (1:1, v/v) dropwise until the solution clears, then add 3 to 4 drops in excess.

Dilute the solution to about 100 ml with water, and transfer to the cell of a high-current mercury cathode electrolysis apparatus. Electrolyze at 15 to 20 amperes until the bulk of the iron is removed. Drain off the solution into a 400-ml beaker, and wash out the cell with a little 1% sulphuric acid from a wash bottle.

Evaporate the solution from the above treatment to dryness, fuming off as much of the sulphuric acid as possible. Cool, wash down the sides with a little hydrochloric acid, and fume again.

Cool, add 100 ml water, and warm to dissolve. Add 10 ml of aluminum chloride carrier solution, and add hydrochloric acid dropwise to clear any turbidity. Add 5 grams of ammonium chloride, bring the solution to a boil, and precipitate the aluminum by the cautious addition of carbonate-free ammonium hydroxide (from a freshly opened bottle) to the hot solution. Digest for 1/2 hour and filter the solution on a fast paper. Wash with a hot 2% solution of ammonium chloride, discarding the filtrate and washings.

Place a clean 250-ml beaker under the funnel and dissolve the precipitate on the paper with 25 ml of hot 10% (v/v) hydrochloric acid. Transfer this solution to a 125-ml separatory funnel. Wash the paper and beaker with further portions of 10% hydrochloric acid and transfer the washings to the funnel as well, to give a final volume of about 50 ml.

Cupferron Separation

To the solution in the separatory funnel, add sufficient saturated potassium permanganate (dropwise with shaking) to impart a permanent pink colour. Cool the funnel to 5°C and add 15 ml of cold, 8% cupferron solution. Mix well, add 15 ml 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, discarding the chloroform each time (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 the rinsings to the flask.

Colour Development

To the volumetric flask add 2 ml of 10% stannous chloride. Stopper the flask and shake well. Add 25 ml of 50% ammonium thiocyanate solution, and mix. Make to volume with distilled water and mix again. Determine the optical density of the solution on the spectrophotometer at 370 mμ, 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 versus optical density for the particular cell path used.

Calculation

$$\% \text{ U} = \frac{\text{mg U (from graph)}}{1000} \times \frac{100}{\text{Sample Wt}}.$$

D. X-RAY EMISSION SPECTROMETRIC METHOD

Outline

Uranium, suitably excited by high-energy x-rays, emits discrete secondary x-radiation which can be measured to give an indication of its concentration in a variety of materials. In the procedure given here, the uranium L_α line is used. A dilution technique, using alumina powder, is employed as an aid in overcoming matrix effects. It is not possible to completely eliminate the effect of other elements, however, so that it is necessary to use standards--either chemically analyzed samples or synthetic mixtures --which closely approximate the composition of the samples being analyzed.

Range

The x-ray emission method permits the determination of uranium down to about 0.05% in carbon steel. Sensitivity will vary slightly in alloy steels due to the matrix effect, and standards used for comparison should have approximately the same composition as the alloy being analyzed.

Apparatus

Equipment for Sample Preparation: (See Figure 14.)

Blender-mill	Pitchford Pica, Cat. No. 3800
Vials, hardened tool steel	Pitchford, Cat. No. 202
Balls, 5/8" dia. tungsten carbide	Pitchford, Cat. No. 306

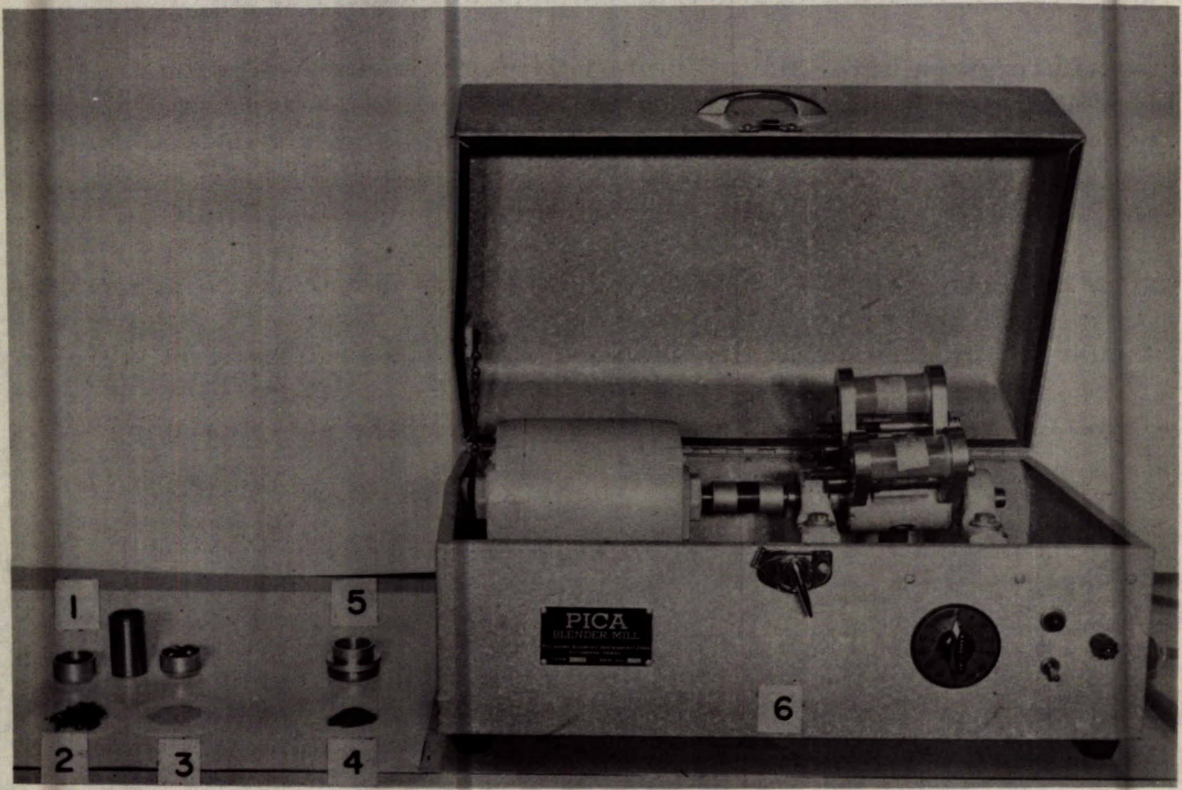

Figure 14. Sample preparation for x-ray emission method.

1. Tool steel vials and tungsten-carbide balls.
2. Steel turnings.
3. Alumina powder.
4. Powdered steel-alumina mixture.
5. Sample holders for x-ray apparatus.
6. Pica blender-mill.

(Apparatus, cont'd)

X-ray Spectrometer, consisting of:

Basic x-ray generator unit, 60 KV-50 mA	Philips Electronics Ltd., Cat. No. 12045/3B.
Molybdenum target x-ray tube	Philips Electronics Ltd., Cat. No. 52360.
Universal all-vacuum x-ray spectrograph attachment	Philips Electronics Ltd., Cat. No. 52130.
Lithium fluoride analyzing crystal	
Electronic circuit panel, including linear amplifier power supplies, scaler-ratemeter assembly, timer and recorder	Philips Electronics., Cat. No. 12096.
Sample containers with Mylar film bottoms	To fit spectrograph.
Mylar film	To cover bottom of sample container.

Reagents

Alumina powder:	Finely ground (-200 mesh).
Plain carbon steel drillings or chips:	Uranium-free for preparation of standards. (Use other types of uranium-free steel to provide the same base alloy as the samples.)
Uranium dioxide powder	Pure uranium dioxide.

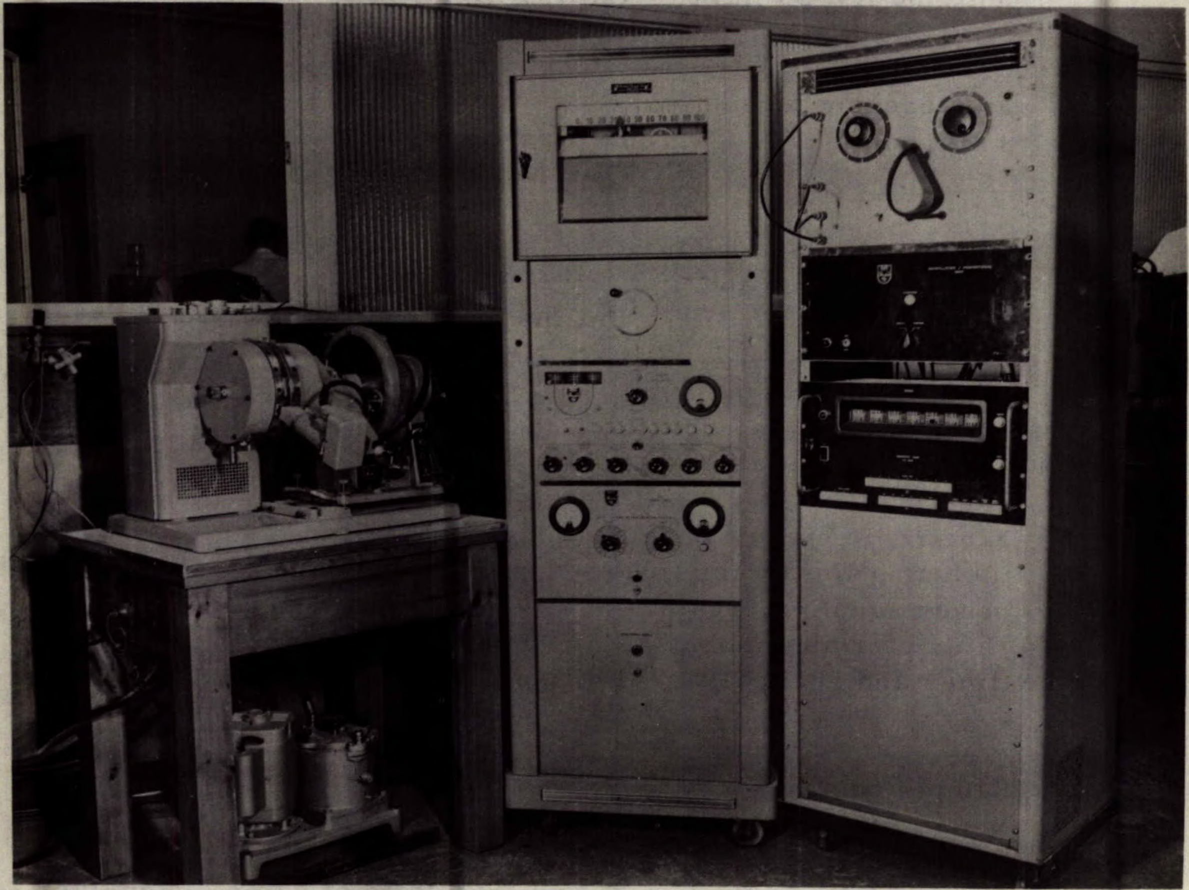

Figure 15. X-ray fluorescence spectrometer.

Preparation of Standard Curve

Weigh a 5-gram sample of uranium-free steel drillings or chips into a hardened, tool steel vial (see Figure 14) and add a carefully weighed 5.6-mg portion of the UO_2 powder. Add 3 grams of alumina powder and two tungsten-carbide balls. Close the vial and shake on the blender until the sample is reduced to a homogeneous powder, corresponding to 5 grams of a steel sample containing 0.1% uranium. Transfer to the spectrometer sample holder and tap down lightly to pack and level off the sample. Place the container in the spectrometer (Figure 15) and rotate it into the counting position. Set the goniometer at the peak of the uranium L_α line ($2\theta = 26.14$ for lithium fluoride analyzing crystal). Use the following power settings on the x-ray tube: voltage, 55kV; current, 45mA. Set the scintillation counter high voltage to the previously determined optimum setting. Record the time required to accumulate 64,000 counts. Move the goniometer off the uranium peak to a nearby background region and count the background. Calculate the net counts per second due to uranium, and record the value. Repeat for other standards similarly prepared, and plot a graph of uranium concentration versus net counts per second.

Note: Uranium dioxide diluted with alumina can be used for the standard addition provided it is well mixed. Alternatively, standard uranium-bearing steels may be used.

Procedure

Weigh out a 5-gram sample. Transfer to a clean tool steel vial. Add 3 grams of alumina powder and two tungsten-carbide balls. Carry out the balance of the procedure as described under "Preparation of Standard Curve". From the net counts per second (corrected for background), read the uranium content from the standard curve.

E. RADIOMETRIC METHODS

Outline

Although the refining process eliminates the highly radioactive daughter elements which are present in uranium ores, it is nevertheless possible to determine the uranium content of steel and alloys at moderately low levels using the weak radioactivity of the uranium itself and of its immediate short-lived decay elements. Both beta- and gamma-ray counting methods are applicable, but since the beta emission is a surface effect whereas the gamma emission originates throughout the sample (for thin specimens), gamma-ray counting will give more reproducible results.

Beta-ray counting uses a beta-sensitive Geiger tube with a one-inch (or larger) diameter window, and a ratemeter or scaler. In view of the fact that beta-ray emission is from the surface only, sample preparation is highly critical.

Gamma-ray counting uses a scintallation detector. A preamplifier which is an integral part of the counting apparatus amplifies the pulses, which are then directed to a single-channel pulse analyzer. This analyzer passes only those pulses in the energy range 60 to 200 keV, thus rejecting most of the energy arising from background radiation.

Since the gamma-radiation being counted is relatively soft, internal absorption within the sample is a factor, and the thickness of the sample pellet should therefore be limited to about 0.25 inch. The chemical composition of the alloy plays a very minor part, but it is often helpful to employ standards of composition similar to that of the samples under tests.

Range

The lower limit of counting methods is largely determined by the level of the background and its variability. This is partly dependent on the instrumentation and partly on location. Under the conditions described here, uranium could be determined down to about 0.01% by both beta and gamma methods. With longer counting times, the background and sample count-rates can be established with greater precision, so that smaller differences can be made statistically significant, thus lowering the limit of sensitivity.

1. The Beta-ray Counting Method

Apparatus

For preparation of the pellet: (See Figure 16.)

Hydraulic press: 24,000 psi capacity.

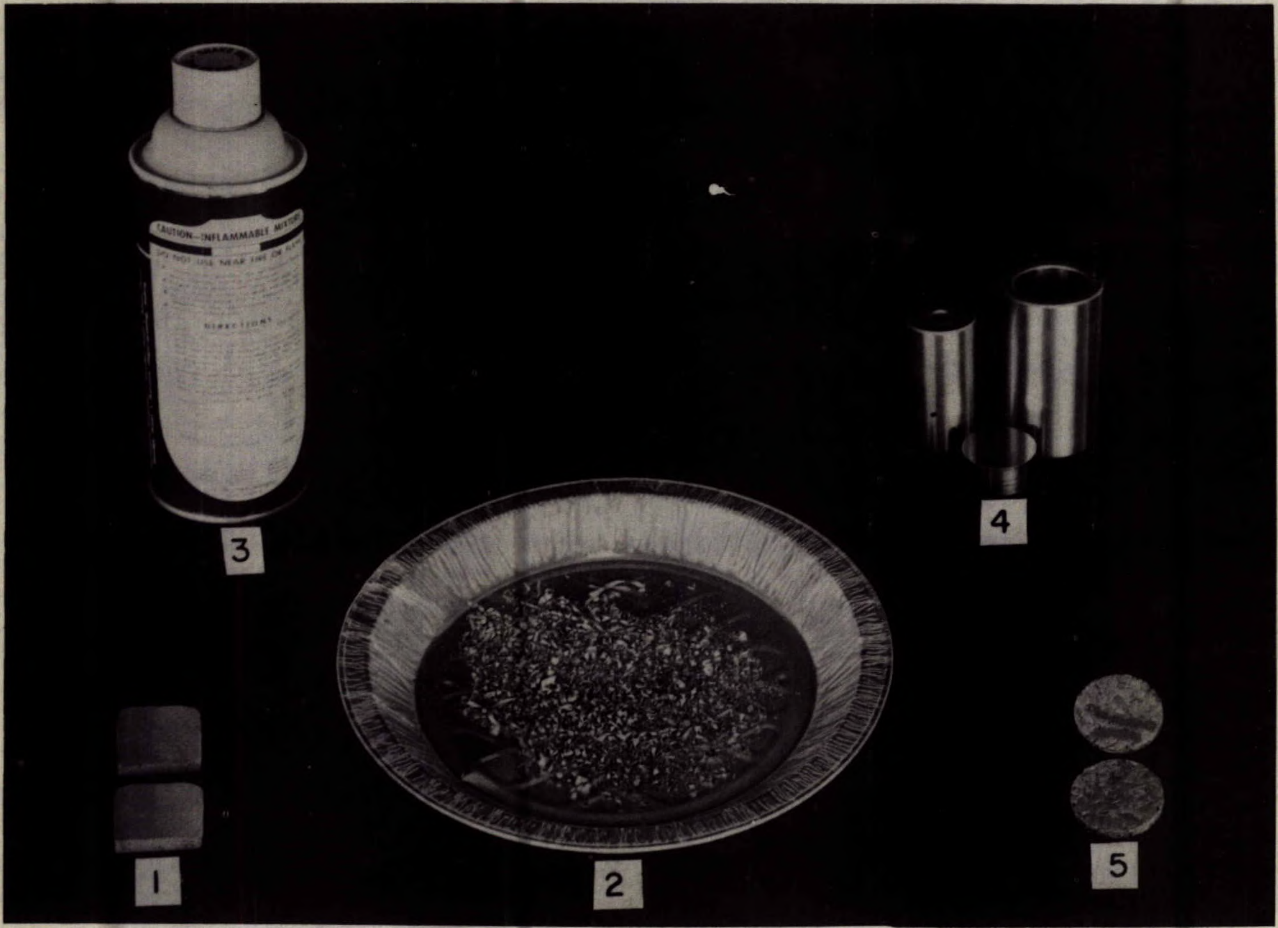

Figure 16. Sample preparation, radiometric method.

1. Slices from steel bars.
2. Steel turnings.
3. Acrylic spray.
4. Cylindrical mould.
5. Compressed pellets formed from sprayed steel turnings.

(Apparatus, cont'd)

Mould, cylindrical:	1.25 in. dia.
Acrylic resin spray bomb:	
Aluminum foil pie plates:	
Infra-red lamp:	
Square end spatula:	

Counting Equipment:

Lead shield or castle, 2-inch wall thickness:	Inner cavity, 3" x 3" x 2", fitted with sliding tray and sliding or hinged lead brick door.
Geiger tube:	e.g. Anton Laboratories 1001-H.
Scaling circuit with high-voltage power supply and timer:	e.g. Nuclear-Chicago, Baird-Atomic Instrument Co., Electronic Associates Ltd., or others.

Pellet Preparation

Weigh out a standard amount, say 20 grams, of sample, in the form of chips or turnings and spread out in a pie plate. Spray the sample with an even, but very thin coating of acrylic resin in a fume hood, and dry under an infra-red lamp. Let cool. Pour the sample into the mould, and press at 24,000 psi at room temperature.

Calibration

Determine the background count rate (counts per minute), by placing a sample, containing no uranium, in the castle and counting for 10 minutes. Next, count a group of samples containing several different uranium concentrations whose values are known by chemical analysis. Count each face of a pellet for 5 minutes and record the count (the period might be as long as 30 minutes if the sample is low in uranium, e.g., $< 0.03\%$ U). Subtract the background count, and plot a graph of the resulting net count rate per minute versus the known per cent uranium concentration. Draw a straight line which passes through the origin and determine from it the sensitivity (measured in counts per minute per 1% uranium). This value will be about 2400, with a background of 20 counts per minute. Use the value for the sensitivity to determine a counting interval which results in a direct reading on the counter dial of the per cent uranium. A scale-of-64 counter produces one "register-pulse" for every 64 pulses from the Geiger tube. Consider the count register to read 1/100 of a per cent. Then count, for $\frac{64 \times 100}{2400}$ or 2.67 minutes, each face of the pellet. Pellets of low uranium content might be counted longer for better accuracy, i.e., 10.67 minutes with a scale of 256, or 26.7 minutes with a scale of 64, considering the count register to read 1/1000 of a per cent uranium.

The background counted for the same interval will have to be subtracted to leave the net per cent uranium from the sample. This background reading is expressed as "equivalent per cent uranium".

Procedure

Prepare a compressed pellet of the sample in the manner described. Insert the pellet in the castle and set the counter-interval timer for the interval which has been found, from the above calibration procedure, to give direct read-out in per cent uranium. Start the counter, and at the end of the automatically-timed interval, read the uranium content directly off the dial, subtracting the background correction. Turn the pellet over, and read the other face in the same manner, Average the two values and report the result obtained.

2. The Gamma-ray Counting Method

Apparatus

Equipment for sample preparation:	See beta-ray method (Figure 16).
Counting equipment:	(See Figure 17.)
Lead shield or castle, 2" wall thickness.	Inner cavity, 4" x 4" x 12" high or to contain detector and sample. Provide with removable top.
Sodium iodide crystal, 2 1/2" x 1/2" diameter, mounted:	Harshaw Chemical Co., Cleveland, Ohio.
Type 6655 photomultiplier tube:	R.C.A., Montreal, P.Q. or Camden, N.J.
Preamplifier:	Nuclear-Chicago Corp., or others.
Single-channel pulse analyzer:	Nuclear-Chicago Corp. Model 132B.

Calibration

An energy calibration standard (Cs-137 at 662 keV) is supplied by the manufacturer of the analyzer. Following the detailed

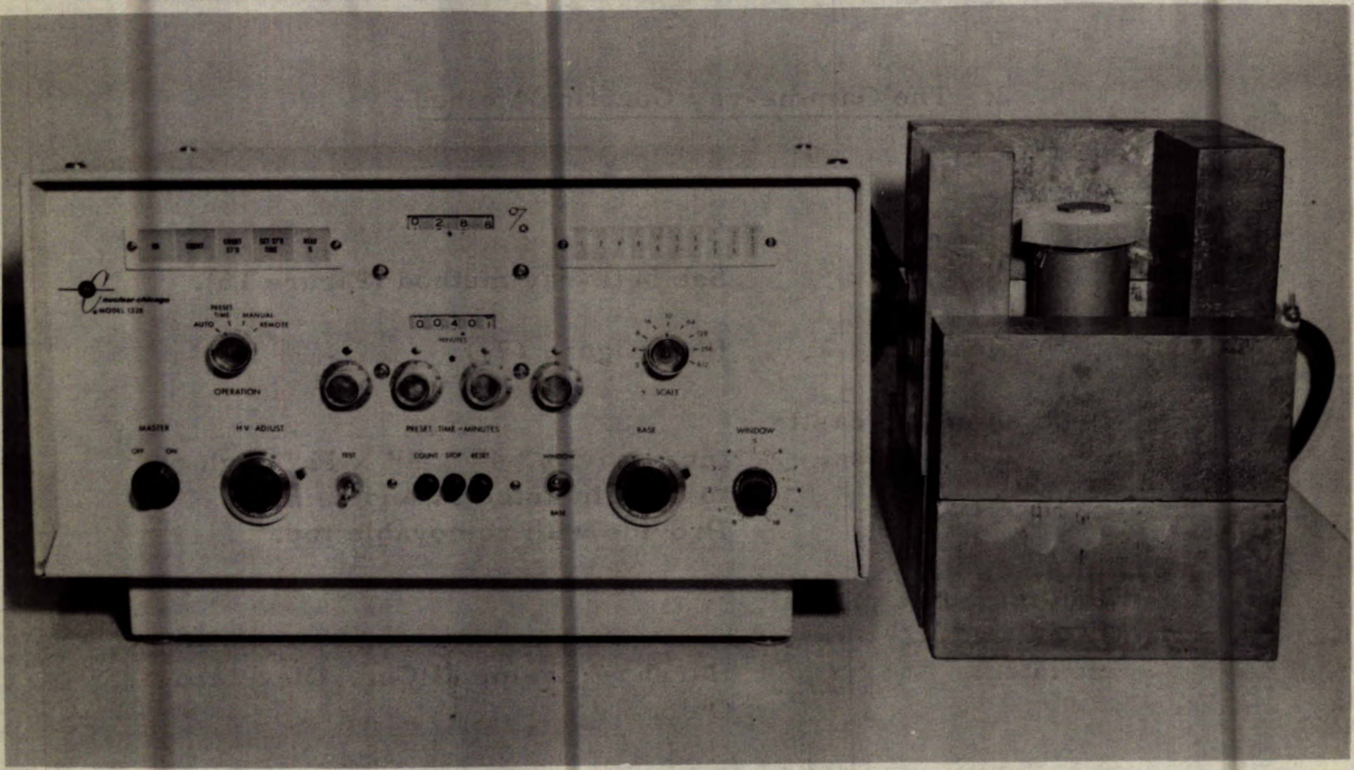

Figure 17. Photograph of gamma-ray assay system.

Left - Scaler, Nuclear-Chicago Model 132-B.

Right - Castle (part of shield removed to show pellet in place on scintillation head).

instructions in the manual, the high voltage is adjusted until the base scale of the analyzer reads directly in kilo-electron-volts. The base is then set to "060" and the window width to "10". The detector will now detect and count gamma-rays in the approximate range of 60 to 160 keV. The analyzer is shown in Figure 17 in a temporary lead castle of 2-inch-thick bricks. The lid has been removed to show a compressed sample mounted on the detector.

When the background count rate has been established, a range of standard size (20-gram) compressed samples (previously assayed chemically) is counted to find a factor stated as "net counts per minute per one per cent uranium". This factor may also require a correction curve where a range of sample weights will be encountered; it is determined empirically for a range of weights, say 10 to 50 grams, with 20 grams as the value 1.000.

The factor, c/min/1% U, is now used to calculate a suitable counting time to have the register dial read directly. In the example pictured, the time was 1.05 minutes, using the "32" scale, and the background was equivalent to 0.012% U. Generally for less rapid, but more accurate, work the time should be 4.2 minutes on the "128" scale, counting once each face of the sample.

Procedure

Prepare a compressed pellet of the sample, in the manner described above. Having calibrated the instrument to read directly in per cent U, as given in the section immediately preceding, place the sample pellet on the detector in the castle. Start the counter, and at the end of the automatically timed period, read the uranium content directly off the counter dial, subtracting the background. Turn the pellet over and count the other face in the same manner. Record the average of the two values and report the result obtained.

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