CANADA

TIN-COLLECTION SCHEME FOR THE DETERMINATION OF THE PLATINUM-GROUP METALS AND GOLD

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TIN-COLLECTION SCHEME FOR THE DETERMINATION OF THE PLATINUM-GROUP METALS AND GOLD

by

G.H. Faye*

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SYNOPSIS

A program conducted in the Mines Branch laboratories on the analytical chemistry of the precious metals has led to the development of a comprehensive scheme for the accurate determination of the individual platinum-group metals and of gold in ores, rocks, and mineralogical and metallurgical concentrates.

In the proposed scheme, the precious metals are collected in molten tin when the sample is fused at 1200-1250°C with a flux containing stannic oxide, sodium carbonate, silica, borax, and powdered coke. The resultant tin alloy is dissolved and the individual precious metals are isolated by ion exchange, distillation and solvent extraction processes.

This report presents the procedural details of the new scheme so that they may be applied readily to materials of a diverse nature in the smaller laboratory which lacks sophisticated and costly equipment such as a spectrograph. With the exception of the usual facilities required in the fusion step of fire assaying, standard equipment can be used in the wet chemical operations for the isolation and determination of the individual precious metals.

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Direction des mines

Rapport de recherches R 154

MÉTHODE DE DOSAGE DES PLATINIDES ET DE L'OR PAR DISSOLUTION DANS L'ÉTAIN

par

G. H. Faye*

RÉSUMÉ

La mise au point d'une méthode d'ensemble pour le dosage précis de chacun des platinides et de l'or dans les minerais, les roches et les concentrés minéralogiques et métallurgiques, a été réalisée dans les laboratoires de la Direction des mines, au cours d'un programme de recherches mené sur la chimie analytique des métaux précieux.

Dans la méthode proposée, l'étain en fusion collecté les métaux précieux quand l'échantillon est fondu à 1200-1250°C. à l'aide d'un fondant contenant de l'oxyde stannique, du carbonate de soude, de la silice, du borax et du coke pulvérisé. On dissout l'alliage d'étain ainsi obtenu, et on isole chacun des métaux précieux par échange d'ions, distillation, et extraction par les solvants.

Le présent rapport donne les détails de la marche à suivre dans cette nouvelle méthode afin qu'on puisse l'appliquer aisément à des matériaux de compositions variées dans le petit laboratoire dépourvu d'équipement coûteux et compliqué comme le spectrographe. On peut utiliser l'équipement habituel au cours de l'analyse par voie humide visant à l'isolement et au dosage de chacun des métaux précieux; il faut en outre disposer de l'installation nécessaire à la phase de fusion au cours de l'essai pyrognostique.

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INTRODUCTION

The literature reveals numerous problems associated with the accurate determination of the individual metals of the platinum group in ores, rocks, and mineralogical and metallurgical concentrates.

Many of the difficulties arise from the use of the time-honoured method of fire assaying in which molten lead is used to collect or sequester the precious metals from the fused sample material. Although this method is undeniably satisfactory for gold and silver, there are many instances where it is unsuitable for the determination of the platinum metals, especially at the microgram level. For an understanding of many of the problems in the classical method of fire assaying (including both the pyrometallurgical and wet chemical operations) as applied to the platinum metals, the interested reader may refer to certain publications by Beamish and co-workers (1-7).

To overcome some of these difficulties, certain of the larger mining and metallurgical laboratories employ spectrographic techniques to analyze precious-metal beads produced in the classical method of fire assaying. Although reliable results can be obtained for platinum, palladium, rhodium, and gold, this approach has been unsatisfactory for iridium, ruthenium, and osmium (8). Further drawbacks to the spectrographic finish, at least for some laboratories, are the cost of equipment and the need for highly trained operators.

Because of the problems indicated above, interest has been aroused in developing methods other than those based on the collection of the platinum metals in lead. Among these are: purely wet chemical methods, neutron activation analysis, and fire assay methods using a metal other than lead as a collector. Although the first two of these approaches are useful in particular situations, they cannot, as yet, fulfil the need for a versatile method that can be used routinely in a modestly equipped laboratory.

In the Mines Branch laboratories, investigations conducted during the past six years have led to the development of a new scheme of analysis that overcomes the major difficulties of existing methods.

The object of this report is to present the procedural details of the new scheme in a unified way such that they may be used readily for the determination of the individual platinum metals and gold in materials encountered in geochemical and mineralogical studies and for routine work in laboratories associated with the production and refining of the precious metals.

In this scheme (Figure 1), the precious metals are collected in molten tin when the sample is fused at 1200-1250°C with a flux containing stannic oxide, sodium carbonate, silica, borax, and powdered coke. The resultant tin alloy is then treated by relatively simple wet-chemical techniques to isolate and separate the individual metals prior to their determination by spectrophotometric (or gravimetric) methods.

The tin-collection scheme has been applied successfully to the determination of one or more of the platinum metals and/or gold in materials such as silicate rocks, copper-nickel ores and concentrates, copper-nickel matte, meteorites of both the iron and stony types, and the minerals magnetite, chromite, and osmiridium.

Gold is included in the new scheme because it is associated with the platinum metals in various mineral assemblages and therefore it is sometimes desirable to determine this element on the same sample that is being analyzed for the platinum metals.

For details of the developmental work involving platinum and palladium (9), rhodium (10), iridium (11), ruthenium and osmium (12), and gold (13), the reader should refer to the cited papers.

GENERAL COMMENTS ON THE ANALYTICAL SCHEME

Certain types of materials, such as copper-nickel matte, precious metals concentrate, meteorites and osmiridium, may necessitate the determination of all six platinum metals plus gold; Figure 1 indicates the steps required for these determinations to be made on a single sample. However, many of the operations can be omitted when only partial analysis is required. For example, it is often necessary to determine only platinum and/or palladium because the abundance of these elements in many materials is usually considerably greater than those of the other precious metals.

There are situations where it may be convenient, and perhaps more rapid, to perform some of the determinations on one portion of sample material (e.g., osmium and/or ruthenium) and proceed simultaneously with the determination of other members of the group on a second portion.

APPARATUS

The apparatus described below is recommended primarily because it proved satisfactory in the author's laboratory; however, it is not necessary to adhere rigidly to the specifications given.

Assay Furnace: 15-kw Globar type with suitable thermocouple and temperature controller. The furnace should be capable of accommodating 6 assay crucibles and maintaining their temperature at 1250°C.

Jelrus Handy-Melt Portable Electric Furnace: This small vertical furnace is equipped with removable graphite crucibles and is used for melting tin-base assay buttons prior to their granulation in water. After 4 to 6 months of relatively constant use, it is recommended that the bottom of the crucibles be examined for small holes.

Spectrophotometer: The spectrophotometer should be capable of making absorbance measurements in the range 300 to 800 mμ.

Distillation Apparatus: The design of the apparatus is shown in Figure 2. Vessel A is a 500-ml round-bottomed distillation flask and receiver B is a 250-ml, two-necked, round-bottomed flask which, during the ruthenium distillation, is fitted with a 250-ml Glas-Col heating mantle. Receivers C and D are 125-ml, tall-form gas washing bottles with fritted cylinders at the end of the inlet tubes. Each fritted cylinder is pierced to make a 1/16-inch hole to permit free flow of gases through the apparatus.

Cation Exchange Columns: It is recommended that both "large" (2.5 x 25 cm) and "small" (1.5 x 15 cm) columns be prepared with water-washed, 20-50 mesh, Dowex 50W-X8 cation exchange resin. Columns of the above dimensions are suitable for the removal of approximately 4 and 0.5 g of combined base metals respectively (mainly copper and nickel).

To remove base metals and regenerate the resin, pass 4 N hydrochloric acid through the column until the effluent solution is free of copper and nickel (test with ammonium hydroxide). Wash the resin with water until the effluent is neutral to litmus paper.

Assay Crucibles: Catalogued as "40-gram" type.

Reagents: Details of the preparation of special reagents will be given under "Methods" in the sections describing their use.

METHODS

A. Pre-Treatment of Sample

Depending upon the nature of the sample, a pre-treatment is frequently required to remove or convert certain constituents to a form that will not lead to difficulties in subsequent operations.

1. Roasting:

This process is used primarily to convert sulphides to oxides, but also to volatilize arsenic and antimony, when present, and thus prevent

the formation of matte or speiss during the subsequent fusion. It is recommended that samples other than alloys and copper-nickel matte be roasted prior to being mixed with the flux.

It is known that osmium (but not ruthenium) is lost by volatilization during the roasting operation. Fortunately, this step can be omitted when certain types of platiniferous materials are to be analyzed for osmium.

Procedure: Place the sample (-200 mesh), weighing up to 1 assay ton, in a shallow fire-clay dish and roast at 750-800°C for approximately 1 hour with intermittent stirring.

In cases where only a few grams of material (particularly sulfides) are to be roasted, place the sample on a thin bed of silica to prevent possible loss of the resultant calcine to the surface of the dish (include the silica used as part of the total quantity required for fluxing (Section B.1). When cool, mix the calcine with the flux and proceed with the fusion process as indicated below in Section B.5.

2. Leaching of Copper-Nickel Matte

This pyrometallurgically produced sulfide can be leached conveniently in the following manner to remove the bulk of the copper and nickel and leave the precious metals in a concentrated form in the leach residue.

Place the sample, weighing up to 2 assay tons, in a 1500-ml beaker and treat with approximately 25 g of ammonium chloride and 100 to 200 ml of 12 N hydrochloric acid. Heat the covered beaker and contents until the amount of insoluble matter appears not to exceed approximately 2 g. When dealing with large sample weights, it may be necessary to retreat the leach residue once or twice with fresh acid after intervening filtrations.

Recover the insoluble matter by filtration through a No. 30 Whatman paper and then dry the residue and paper in a drying oven.

When the dried residue is to be analyzed for osmium, mix it with the flux for fusion in the manner described in Section B below; otherwise it is preferable to roast the material as in Section A.1.

3. Acid Attack of Metallic Phase from Meteorites

Because the determination of the platinum metals in meteorites (especially in the metallic phase) is of geochemical interest, a procedure for handling this kind of material is included here.

The meteoritic iron-nickel alloy would not be attacked appreciably during the fusion process, because of the relatively low temperature and the reducing conditions that prevail. However, this problem can be avoided by dissolving the alloy in hydrochloric acid and then fusing the resultant chloride salts as in Section B below. The net result is to slag off the iron and collect the precious metals in the tin button.

Procedure: Dissolve the meteoritic alloy (preferably more than 5 g of granules or turnings) in a requisite amount of boiling 12 N hydrochloric acid. Evaporate the solution to dryness directly on the hot-plate and near the end of the operation stir the crystallizing salts with a glass stirring rod. The heating should be carried out in such a way as to drive off as much free acid as possible yet keep the mass from baking and thus lessen the possible danger of losing osmium as the volatile tetroxide.

Scrape the dried salts from the beaker and add to the flux as described in Section B.5 (a). Using small portions of water and a rubber policeman, dissolve and dislodge the remaining material adhering to the beaker and pour the solution (suspension) into a bed of the standard flux (Section B).

B. Crucible Fusion Process (Preparation of Buttons)

1. Flux

The flux that has proven most satisfactory for nearly all materials so far encountered, contains the following materials in the indicated quantities:

		g
SnO_2	-	35
Na_2CO_3	-	50
SiO_2	-	10-20
$Na_2B_4O_7$	-	10
Coke	-	5-8
Approx.	-	120

The quantities of silica and coke are adjusted according to the amount of silica and iron, respectively, in the sample (for details see Section B.4 below).

Using 120 g of the above flux, and samples weighing up to 1 assay ton, tin buttons weighing approximately 20 g are obtained. This represents about 70 per cent recovery of the tin, the remainder being slagged off.

2. Amount of Sample Required for Analysis

Usually the analyst has some prior knowledge of the range of platinum metals and base metals values to be expected and can make a choice of sample weight according to the following considerations.

Using the spectrophotometric methods described in a later section of this report, the smallest amounts of the individual precious metals that can be determined with reasonable accuracy are: approximately 3 micrograms of each of platinum, palladium, rhodium, iridium, ruthenium and gold, and approximately 10 micrograms of osmium.

To determine smaller quantities of the precious metals than indicated above, replicate buttons from 1-assay-ton samples can be combined and analyzed according to the wet chemical methods to be described.

3. Behaviour of Copper and Nickel During Fusion

During the crucible fusion process, virtually all of the nickel and copper in the charge form an alloy with the tin, while the iron remains in the silicate slag. Experience has shown that it is desirable to keep the combined nickel and copper content of the button to less than approximately 4 g.

Copper and, particularly, nickel increase the melting point of the assay button. Therefore, when more than 1-2 g of the base metals are expected to be present, approximately 10 g of tin (stick-tin is a convenient form) can be added to the charge to reduce the melting point of the button and thus facilitate the granulation process (Section B.5 (c)).

4. Variation of Composition of Flux with Nature of Sample

In contrast to the classical method of fire assaying, the flux and the proposed fusion process need not be modified greatly when processing materials of a diverse nature. However, minor variations in the charge are made with certain types of materials; these are indicated below, together with a general description of the kinds of material to which the proposed analytical scheme may be applied.

Siliceous Ores and Rocks: With a 1-assay-ton sample of such materials, the quantity of silica used in the flux may be varied from 20 to 10 g, depending on the estimated silica content of the sample.

Platiniferous rocks are frequently of the ultra-basic type such as dunite, pyroxenite, etc., and these contain the precious metals in minute, widely dispersed blebs of native platinum or perhaps osmiridium.

Because of the heterogeneity of such rocks, reproducible results may not be obtained.

Magnetite and Chromite: The relatively large amount of oxidized iron and/or chromium in these materials to be reduced to lower oxidation states requires the use of approximately 8 g of coke in the fusion of a 1-assay-ton sample. Usually platinum is the predominant precious metal in these minerals.

Copper-Nickel Sulfide Ores and Concentrates: Because of the relatively large amounts of base metal oxides that may be present (after roasting) and must undergo reduction, 6 or 7 g of coke is required in the fusion of a 1-assay-ton sample.

Copper-nickel sulfide ores are among the most commonly encountered naturally platiniferous materials. Although minute grains of platinum metal-bearing minerals, such as sperrylite ($PtAs_2$), michenerite ($PdBi_2$) and froodite ($PdBi_3$), are known to occur in these sulfides, it is considered by some workers that the platinum metals are present, not as discrete compounds or minerals, but, rather, in solid solution in the base metal minerals pentlandite, pyrrhotite and chalcopyrite.

All members of the platinum metals group are known to occur in certain copper-nickel sulfide deposits; however, palladium and sometimes platinum are the predominant metals. Other members of the group are usually less abundant by a factor of 5 to 10.

Osmiridium (Iridosmine): This native alloy, as the name suggests, is composed mainly of osmium and iridium and occurs in placer deposits in the form of flattened grains. Osmiridium is among the most chemically inert minerals known. However, it seems to be completely attacked during the crucible fusion process (11, 12) of the proposed analytical scheme, thus lending itself to accurate analysis.

Gold Content of Stannic Oxide (13): The batches of stannic oxide analyzed by the author contained from 0.1 to 0.2 ppm of gold. Therefore it is imperative that the gold value of each batch of stannic oxide be determined and subtracted as a blank when the determination of gold (Figure 1 and Section D.8) is included in the analytical scheme.

5. Procedure for Preparation of Buttons:

a) Mixing the Charge

Dry samples: Follow the standard assay practice by blending the dry samples with the flux on glazed paper and transfer the charge to a "40-gram" assay crucible.

Wet samples: When solutions or suspensions (e.g. from acid decomposition of meteorites) are to be mixed with the flux, place approximately one third of the standard flux in the crucible and press a square of "Saran" film into the crucible to form an envelope, and into this envelope transfer the remainder of the flux. With a spatula, form a cavity in the bed of flux and transfer the sample slowly into the depression so as to avoid wetting the film or crucible walls. Heat the crucible and contents in a drying oven at 110°C for at least 2 hours. After the sample has dried, remove the material in the Saran envelope and grind it in a mortar, mix well, and place back in the film in the crucible.

b) Fusion: Place the crucible in an assay furnace maintained at approximately 1250°C and fuse the contents for 1 hour. During the first 15 minutes inspect the crucibles several times to ensure that evolution of gases, or frothing, is not excessive. On the few occasions when this situation arises, swirl the molten material in the crucible several times with tongs until the melt becomes quiescent, then continue the fusion.

At the completion of the fusion period the melt should not be viscous or lumpy, nor should there be extensive crust formation at the top of the melt. When evidence of refractory constituents is found, it may be necessary to repeat the fusion with a new portion of sample material after making appropriate adjustments in the proportions of coke and/or silica in the flux.

Pour the melt into a conical steel mould, and when cool, separate the tin button from adhering slag by tapping with a small hammer. (A small file can sometimes be used to advantage in removing tenaciously adhering encrustations of slag, but loss of metal should be avoided.)

c) Granulation of Button: Place the button in the graphite crucible of the Jelrus furnace (see page 3), from which air is purged by nitrogen gas delivered through a suitable ceramic tube placed directly over the button. After melting the button (which may require a temperature of 600-700°C for buttons rich in nickel particularly), withdraw the nitrogen delivery tube and, using tongs to hold the crucible, quickly pour the molten tin-alloy into approximately 1 gallon of water contained in an enamel pail. Decant the water; dry the alloy on the hot plate (avoid re-melting). Any large lumps produced in the above operations can easily be reduced in size with metal shears.

Reserve the granulated alloy for analysis according to the scheme outlined in Figure 1.

C. Wet Chemical Procedures for Isolation and Separation of Precious Metals

1. Isolation of Osmium by Distillation (12)

Place the granulated tin button (Section B.5 (c) above) in a 500-ml distillation flask. For every gram of alloy taken, add approximately 5 ml of 12 N hydrochloric acid. Connect the flask to the distillation apparatus (Figure 2) in which receivers B, C, and D contain 25, 40 and 15 ml of concentrated hydrobromic acid respectively. Receiver C is cooled in an ice bath. Bubble nitrogen gas through the reaction mixture at the rate of 2 to 3 bubbles per second, and then force 30 per cent hydrogen peroxide through the delivery funnel in relatively small portions by "pumping" with the moistened heel of the palm while the stop-cock is alternately opened and closed by the other hand.

During the addition of peroxide, the gas pressure in the apparatus tends to decrease; therefore, it is necessary occasionally to increase the flow of nitrogen temporarily to prevent the receiver solutions from "backing-up".

After the tin alloy has been decomposed, add a slight excess of hydrogen peroxide, apply heat and evaporate the solution in the flask until its temperature rises to 115-118°C. While maintaining the temperature in this range, add approximately 15 ml of 30 per cent hydrogen peroxide in small portions in the manner described above. Next, add rapidly 30 to 35 ml of 12 N hydrochloric acid through the funnel and continue the distillation until the temperature again reaches 115°C. To ensure complete distillation of osmium, repeat the alternate addition of 15 and 30 ml of peroxide and hydrochloric acid, respectively, two more times with the intervening evaporations necessary to bring the temperature to at least 115°C before adding the peroxide.

After heating has been discontinued and the apparatus allowed to cool somewhat, disconnect the receivers and combine their solutions in a 400-ml beaker containing approximately 35 ml of concentrated hydrobromic acid and approximately 25 mg of sodium chloride.

When the samples are known to contain more than 300 µg of osmium, dilute the combined receiver solutions to a known volume with hydrobromic acid and take an aliquot for the determination of osmium.

Evaporate the solution first at a low heat to prevent violent evolution of bromine; then take it to incipient dryness (without baking) at a more rapid rate. Determine the osmium content of the residue spectrophotometrically in the manner described in Section D.7.

When other precious metals in the original button are to be determined, reserve the solution remaining in the flask after the distillation of osmium and proceed with the appropriate part of the analytical scheme (Figure 1).

2. Parting of Tin Button (When osmium is not to be determined)

Transfer the granulated tin alloy to a 600-ml beaker and treat with approximately 150 ml of concentrated hydrochloric acid. Cover the beaker with a watch glass and heat until the alloy has been decomposed and vigorous evolution of bubbles from the black insoluble residue has ceased. Dilute the resulting suspension to about 400 ml with water and heat to 70°C. While the suspension is being stirred with a motor-driven polyethylene-coated stirrer, sprinkle approximately 5 g of powdered tin (-200 mesh or finer) into the beaker to precipitate any precious metals that had dissolved during the parting operation. After stirring for about 15 minutes, again heat the beaker and contents to 70°C and add a second 5 g portion of powdered tin, as before, with an additional stirring period of 10 to 15 minutes.

The insoluble matter produced in these operations contains essentially all the copper in the sample, the excess tin powder, and all of the precious metals. Nickel remains in solution and is ultimately discarded.

Decant the supernatant solution through a pad of paper pulp (from Whatman No.31 paper) supported on a filter disk. Wash the solids several times by decantation with 1 N hydrochloric acid and pass the washings through the filter pad.

Add approximately 50 ml of 12 N hydrochloric acid to the solids in the beaker, and then cautiously add 30 per cent hydrogen peroxide in small portions until the solids have dissolved and excess peroxide is present. After the beaker has been heated for a few minutes to ensure complete dissolution of the residue, place it under the filter pad and wash the pad with approximately 20 ml of a 3 to 1 mixture of 8 N hydrochloric acid and 30 per cent hydrogen peroxide to dissolve any fines caught on the filter during decantation.

3. Volatilization of Tin

Evaporate the solution to a relatively small volume on the hot plate, then place the beaker in an aluminum "no-bump" solution evaporator. Heat the evaporator from below with the hot plate and from above with an infra-red heat lamp to volatilize as much tin as possible.

Copious fumes of stannic chloride are evolved at this point and, when relatively large amounts of copper and/or nickel are present, care should be taken to avoid spattering caused by local intense heating.

When it appears that the evolution of fumes has nearly ceased, remove the beaker from the evaporator and cool for a short time. Wash down the sides of the beaker with approximately 10 ml of a 7 to 2 mixture

of hydrochloric and hydrobromic acids and again evaporate to dryness under the heat lamp. Repeat both the treatment with the mixed halogen acids (5-10 ml) and the evaporations twice, or until it is evident that essentially all of the tin has been volatilized.

If gold is to be determined, simply evaporate the mixed halogen acid solution as in Section C.4 below.

If gold is not to be extracted, cool the beaker and residue, add 10-15 ml of 12 N hydrochloric acid, and then, while swirling the beaker in a fume hood, cautiously add 30 per cent hydrogen peroxide until it is evident that an excess of peroxide is present and that the evolution of bromine vapour is not vigorous. Evaporate the solution to a small volume and process according to requirements (see flow sheet) for the removal of base metals or the extraction of gold and/or the distillation of ruthenium.

4. Isolation of Gold by Extraction (13)

(Note: If less than 100 µg of gold is expected to be present and its determination is not required, the following extraction procedure can usually be omitted. Experiments have shown that 100 µg or less of gold does not interfere in subsequent operations in the analytical scheme.)

Evaporate the solution from Section 3 above to 2-3 ml. Place the beaker in a hot water bath and, with the use of a jet of compressed air, evaporate the solution gently to dryness.

Take up the salts in 5 ml of 2 N hydrobromic acid and wash into a 60-ml separatory funnel with a further 10 ml of 2 N hydrobromic acid. Extract the gold by shaking the solution with two separate 15-ml portions of diethyl ether. (Double the volume of hydrobromic acid and ether when the sample contains a relatively large quantity of copper.) Combine the ether extracts and wash with three separate 5-ml portions of 2 N hydrobromic acid.

Evaporate the aqueous phase to dryness and, with a small volume of 2 to 1 hydrochloric acid and 30 per cent hydrogen peroxide, destroy bromides and convert the metals to their chloro-complexes. Reserve the resulting solution for the determination of the platinum metals according to the procedures given below.

Strip the gold from the ether phase by shaking it with three separate 15-ml portions of water. Treat the aqueous gold solution with approximately 50 mg of sodium chloride and 5 ml of aqua regia, and evaporate on the hot plate to approximately 2 ml. Reserve the solution for the spectrophotometric determination of gold (Section D.8.).

5. Isolation of Ruthenium by Distillation (12)

(Note: The following procedure is generally applied directly after the tin volatilization step. However, when the sample solution contains more than about 2 g of base metals and it is to be analyzed subsequently for one or more of platinum, palladium, rhodium and iridium, then it is recommended that the base metals be removed by cation exchange (Section C.7 below) prior to the perchloric acid distillation of ruthenium. By using this approach, the subsequent task of decomposing relatively large amounts of perchlorates is avoided.)

Evaporate the solution to dryness on the hot plate to drive off as much free hydrochloric acid as possible. Cool the beaker, take up the residue in a small volume of water, and transfer to a 500-ml distillation flask by washing with several small portions of water. Connect the flask to the distillation assembly (Figure 2) in which Receiver B contains a saturated potassium permanganate solution, prepared by mixing 2 g of solid permanganate and 25 ml of water; Receivers C and D contain 40 and 15 ml of concentrated hydrobromic acid respectively. Cool Receiver C in an ice bath. While nitrogen is bubbled through the apparatus at the rate of 2 to 3 bubbles per second, add about 50-ml of perchloric acid through the delivery funnel and apply heat to both the distillation flask and the permanganate receiver with their separate heating elements. Continue heating until the reaction mixture boils and the white fumes disappear (about 30 minutes). Boil the permanganate receiver solution (essentially a trap for perchloric acid) vigorously until its volume is approximately 10 to 15 ml; then shut off and remove the heating mantle.

Combine the hydrobromic acid receiver solutions, treat with about 25 mg of sodium chloride, and evaporate the whole solution or an aliquot thereof just to moist salts prior to the spectrophotometric determination of ruthenium (Section D.6.).

6. Removal of Perchloric Acid (Only after ruthenium distillation)

Transfer the perchloric acid solution from the ruthenium distillation to a 600-ml beaker and heat strongly to drive off as much free perchloric acid as possible. Stir the residue with a small volume of 1 to 1 hydrochloric acid and again evaporate to dryness. Repeat these operations until most of the perchlorates have been destroyed (as evidenced by the absence of white fumes).

To ensure that the platinum metals are in a soluble form, treat the residue with approximately 15 ml of aqua regia, heat, and evaporate to dryness in a covered beaker. Remove the watch glass and, by repeated additions of 12 N hydrochloric acid and subsequent evaporations, convert the

metals to their chloro salts.

7. Removal of Base Metals by Cation Exchange (14, 15, 16)

Evaporate the solution of metal chlorides to dryness. When more than approximately 0.5 g of base metals (usually copper) is present, stir the crystallizing salts with a stirring rod to aid in the removal of free hydrochloric acid. Cool the beaker and, depending on the amount of base metals estimated to be present, add 0.25 or 0.50 ml of 12 N hydrochloric acid and then dissolve the salts with 50 or 100 ml of water, to give a solution with a pH of 1.0-1.5.

(Note: At this point the analyst should be aware of the possibility of hydrolysis of the anionic chloro-complexes of rhodium, iridium, and especially ruthenium, during the ion exchange process. In the operating time required, hydrolysis can be prevented by maintaining the chloride ion concentration at 0.1 M or higher, which is normally provided by the base metal salts present. However, when it is apparent that they are in low concentration, it is advisable to add approximately 0.5 g of sodium chloride per 50 ml of solution.)

Pass the sample solution through a cation exchange column at the rate of approximately 5 ml per minute. If the sample contains less than approximately 0.5 g of base metals, use a "small" column; otherwise use a "large" column as described under Apparatus. Collect the effluent solution in a 400-ml beaker and wash the column with sufficient dilute hydrochloric acid solution (pH approx. 1) to quadruple the original volume of the sample solution.

To the effluent solution add approximately 25 mg of sodium chloride and 10 ml of 12 N hydrochloric acid and reserve for the separation of platinum, palladium, rhodium and iridium or the isolation of ruthenium by distillation (see flow sheet).

Notes: (1) In certain cases it may become apparent, from the colour developed during the subsequent evaporation of the effluent solution, that leakage of base metals has occurred. Obviously, it is necessary to repeat the cation exchange operation (using the small column) to remove the contaminants.

(2) If tin was not completely volatilized in earlier steps, it will precipitate in a gelatinous or flocculent form during the ion exchange process and may contaminate both the resin bed and the effluent solution. When the amount of precipitate is relatively small (slightly cloudy suspension), then the danger of losing platinum metals by occlusion or co-precipitation is slight, and therefore any solid material retained on the resin bed can be neglected. The small amount of tin in the effluent can be

removed ultimately by repeating the volatilization procedure given above in Section C.3. When more than a few mg of tin appears to be present, then strip the column with 4 N hydrochloric acid and combine the stripping solution with the original effluent and treat the whole as above for the volatilization of tin before repeating the ion exchange procedure.

8. Separation of Platinum, Palladium, Rhodium and Iridium by Solvent Extraction (17)

Special Reagents:

Equilibrated Tri-n-butyl Phosphate (T.B.P.): Prepare by shaking the purified grade of T.B.P. with an equal volume of 6 N hydrochloric acid in a separatory funnel for approximately 1 minute.

Buffer Solution, pH 2.2: Prepare by mixing 50 ml of 4 M sodium acetate (33 g/100 ml) with 53 ml of 4 M hydrochloric acid.

Ethanolic Solution of p-nitrosodimethylaniline, 0.5%: Mix 0.5 g of p-nitrosodimethylaniline with 100 ml of 95 per cent ethyl alcohol, allow to sit overnight (or place in an ultra-sonic bath for a few minutes); mix again and then filter off any solids on a No.30 Whatman paper.

a) Separation of Platinum and Palladium from Rhodium and Iridium

Evaporate the sample solution, containing a mixture of the platinum metals as their chloro-complexes, from Section C.7. above, to incipient dryness in the presence ot a few mg of sodium chloride. Dissolve the salts in 10 ml of 6 N hydrochloric acid and transfer the resultant solution to a 60-ml separatory funnel by washing with an additional 10-ml portion of 6 N hydrochloric acid. Shake the sample solution with 5 ml of an aqueous 4 per cent (w./v.) solution of sodium iodide and allow the mixture to stand for approximately 0.5 hour. Extract the platinum and palladium iodide complexes with two separate 15-ml portions of a 15 per cent solution of T.B.P. in hexane. Withdraw the aqueous phase, wash it with 10 ml of hexane in a separate funnel, and then reserve it for the separation of rhodium and iridium as in Section C.8.(d) below.

Combine the T.B.P. hexane extracts and strip the mixture of platinum and palladium by shaking it with three separate 10-ml portions of concentrated nitric acid for approximately 30 seconds each. Place the nitric acid stripping solution in a separatory funnel, dilute with an equal volume of water, and shake with 10 ml of hexane to wash out as much T.B.P. as possible.

If the sample solution is expected to contain 50 µg or less of palladium, transfer it to a beaker and treat as in Sections C.8.(b) and C.8.(c) for the determination and/or separation of palladium. When the

sample solution is expected to contain more than 50 µg of palladium, dilute it to a known volume and remove a suitable aliquot for the separate determination of palladium. In the latter case, place both the aliquot and the remainder of the solution in separate beakers and treat as in Procedure C.8. (b).

b) Determination of Palladium with p-Nitrosodimethylaniline (18)

Treat the platinum-palladium solution obtained in Section C.8. (a) with a few mg of sodium chloride and evaporate to incipient dryness. To convert platinum and palladium to their chloro-complexes, add 2 to 3 ml of 12 N hydrochloric acid, evaporate the solution just to dryness, then repeat these operations twice. Add 2 ml of the sodium acetate-hydrochloric acid buffer solution (Section C.8. (a)) and approximately 10 ml of water to the residue in the beaker. Warm the mixture gently for a few minutes and, with the aid of a rubber policeman, loosen any sticky deposits that may be adhering to the bottom of the beaker.

When palladium is to be determined (in the whole sample solution or aliquot thereof), add 1 ml of the 0.5 per cent solution of p-nitrosodimethylaniline and transfer the red solution to a 50 ml volumetric flask. Wash the original beaker with 15 ml of 95 per cent ethyl alcohol, add the washings to the flask, and dilute to volume with water. Measure the absorbance of the solution at 525 mµ, and then determine the palladium content of the sample by reference to a calibration curve prepared from spectrophotometric data obtained from standard solutions that have been taken through the T.B.P. extraction procedure.

c) Separation of Palladium from Platinum

(Note: This separation is based on the fact that at room temperature platinum does not react appreciably with p-nitrosodimethylaniline (18) and thus it remains in the aqueous phase when the palladium-p-nitrosodimethylaniline complex is extracted with chloroform.)

Combine that portion of the solution, taken for spectrophotometric measurement, with the remainder of the solution and transfer the whole to a 60-ml separatory funnel and reserve for the separation of palladium from platinum. When the sample contains 50 µg or more of palladium, and an aliquot has been taken from it for the separate determination of palladium, add 2 ml of the p-nitrosodimethylaniline reagent and 15 ml of ethyl alcohol, and transfer the mixture to a 60-ml separatory funnel.

Extract the palladium-p-nitrosodimethylaniline complex with two or three separate 10-to 15-ml portions of chloroform. If mg amounts of palladium are to be separated, add an additional 1 to 2 ml of p-nitrosodimethylaniline reagent and continue the extraction with further portions

of chloroform until the aqueous phase is light yellow to colourless (see Section D.2. below).

Filter the aqueous phase (or aliquot thereof) through a Whatman No.31 paper into a 400-ml beaker, add approximately 2 ml of concentrated sulfuric acid and approximately 5 ml of concentrated perchloric acid. Reserve this solution for the spectrophotometric determination of platinum according to Section D.3. (a).

d) Separation of Iridium from Rhodium

Transfer the rhodium-iridium fraction obtained in Section C.8. (a) to a 250-ml beaker, evaporate nearly to dryness, and treat with a few drops of concentrated nitric acid to destroy iodides. Convert the rhodium and iridium to chloro-complexes by the repeated addition and evaporation of 2-to 3-ml portions of 12 N hydrochloric acid. Take up the final residue of salts with 5 ml of 6 N hydrochloric acid and 1 ml of 30 per cent hydrogen peroxide (to ensure that iridium remains in the quadrivalent state) and wash the resultant solution into a 60-ml separatory funnel with an additional 5 ml of 6 N hydrochloric acid. Add 5 ml of equilibrated T.B.P. and 5 ml of hexane and shake the funnel and contents for 1 minute. Transfer the lower aqueous phase to a second funnel and repeat the extraction step. Drain the aqueous phase into a clean separatory funnel, wash with approximately 10 ml of hexane, and reserve for the determination of rhodium (Section D.4. below).

Combine the two T.B.P. hexane extracts in a separatory funnel and strip the mixture by shaking it with three separate 15-ml portions of 1 to 9 hydrochloric acid. Reserve the combined strippings for the spectrophotometric determination as in Section D.5 or treat for the removal of ruthenium as in Section C.8 (e).

e) Removal of Ruthenium

If ruthenium is present in the sample material and was not removed previously by the distillation procedure given in Section C.5, it will accompany iridium through the T.B.P. extraction step and subsequently interfere in the spectrophotometric determination of iridium. In such cases treat the hydrobromic acid stripping solution with approximately 1 ml of concentrated sulfuric acid and evaporate the solution to fumes of sulfur trioxide. To volatilize ruthenium, add approximately 1 ml of concentrated perchloric acid dropwise, with swirling, to the fuming solution. After the excess perchloric acid has evaporated, cool the solution, take up in approximately 10 ml of hydrobromic acid, and boil in a covered beaker to a small volume to ensure that iridium is present as its bromo-complex.

D. Spectrophotometric Determination of the Individual Platinum Metals and Gold

For most purposes, in the context of the present analytical scheme, spectrophotometric methods are the most convenient for the determination of microgram and even mg quantities of the precious metals. However, when macro quantities (e.g. from precious metals concentrate) are to be determined, it may be preferable to use gravimetric or electro-analytical methods.

The spectrophotometric procedure described below are in most cases taken directly from the cited literature and are presented because they gave satisfactory results during the development of the proposed analytical scheme.

1. Calibration Curves and Standard Solutions of Precious Metals

It is recommended that spectrophotometric calibration curves (absorbance vs concentration) be prepared from data obtained from standard solutions of the individual precious metals that have been taken through the final steps of the various separation procedures (i.e. extractions, acid treatments, evaporations, etc.), so that their history will be similar to the unknown solutions undergoing analysis.

Information on the preparation and standardization of stock solutions of the precious metals can be obtained from the papers cited in the text of this report.

2. Determination of Palladium

The procedure for the spectrophotometric determination of palladium with p-nitrosodimethylaniline was given in Section C.8 (b) above, because the reagent is also used for the separation of palladium from platinum and the two operations are intimately associated with each other.

When mg amounts of palladium are to be determined, the author recommends the very reliable but less sensitive potassium iodide method (19, 20). This method can be used to analyze the chloroform extracts (Section C.8 (c)) of the palladium-p-nitrosodimethylaniline complex after appropriate treatments.

3. Determination of Platinum

Reagents:

1 M Stannous Chloride Solution (2 M HCl) – prepare by dissolving

22.5 g of $SnCl_2.2H_2O$ in 16 ml of 12 N hydrochloric acid (warm if necessary) and dilute to 100 ml with water.

T.B.P. in hexane, 5% – prepare by diluting 10 ml of T.B.P. to 200 ml with n-hexane.

a) Colour Development in Aqueous Medium (21) (greater than 100 µg

Evaporate the platinum solution from Section C.8 (c) at relatively high heat, until perchloric acid has been driven off and the less dense fumes of SO_3 appear. Cool the beaker and cautiously wash down the sides with approximately 5 ml of 12 N hydrochloric acid. Cover the beaker with a glass and boil the contents vigorously for a few minutes; remove the cover-glass and continue heating just to the point where it is evident that most of the hydrochloric acid has been driven off. Remove the beaker from the hot plate, quickly add 5 ml of 12 N hydrochloric acid and 10-15 ml of water, and cool the sample solution to room temperature in running water.

If the sample solution is expected to contain more than 100 µg of platinum, add 10 ml of 1 M stannous chloride solution, transfer the mixture to a 50-ml volumetric flask, and dilute to the mark with water. Measure the absorbance vs water or a reagent blank of the solution at 405 mµ and subsequently determine the platinum content of the sample.

b) Extraction of Platinum Complex with T.B.P. (9) (Less than 100 µg of Pt)

When it is expected that the sample solution contains less than 100 µg of platinum, treat the solution as in (a) above to the point where hydrochloric acid and water have been added, then transfer to a 60-ml separatory funnel and dilute to 45 ml with water. Add, by pipette, 5 ml of 1 M stannous chloride solution and 10 ml of 5 per cent T.B.P. in hexane. Extract the platinum by shaking the funnel and contents for 1 minute. Discard the lower aqueous phase and centrifuge the extract to remove water droplets. As quickly as possible, transfer the T.B.P. hexane extract to a dry 1-cm cell (a 3-4 ml medicine dropper is convenient) and measure its absorbance against a reagent blank at a wave-length of 350 mµ (see Note 2).

The absorbance of the extract increases fairly rapidly during the first few minutes; therefore, note the absorbance values after intervals of approximately 30 seconds and record the maximum value to which these converge for purposes of determining the platinum content. The absorbance of the extract remains constant for at least five minutes and thus sufficient time is available for handling several samples.

Note 1: In the above procedure the Pt-$SnCl_2$ complex that is formed in the aqueous medium is extracted with T.B.P. Although this can be considered an extension or modification of the method of Ayres and Meyer (21), it should be noted that the absorbing species contains coordinated T.B.P.

The Pt-$SnCl_2$ - T.B.P. complex exhibits a broad absorbance band with a maximum at 310 mμ. However, because of the relatively high sensitivity at this wave-length and the restricted spectral range of some spectrophotometers, the arbitrary wave-length of 350 mμ is recommended for most applications.

Note 2: Experiments have shown that, using the extraction procedure (b), up to approximately 100 μg of gold will not interfere in the determination of platinum. Therefore, the extraction of gold as in Section C.4 can be omitted if gold is not to be determined and if less than 100 μg are expected to be present.

4. Determination of Rhodium (22)

Reagent:

Stannous Bromide Solution, 20% - prepare by placing 10 g of stannous oxide in a 250-ml beaker, together with 35 ml of concentrated hydrobromic acid (redistilled), and heat with constant stirring until the resulting solution is clear. Cool the solution and dilute to 50 ml with concentrated hydrobromic acid. The reagent solution should be prepared fresh daily.

Colour Development:

Evaporate the rhodium solution from Section C.8 (d) above, just to dryness, treat with several ml of aqua regia, reconvert the rhodium to its chloro-complex by the repeated addition of 12 N hydrochloric acid and intervening evaporations, and finally evaporate just to dryness. Cool to room temperature, add 5 ml of water, 10 ml of 70 per cent perchloric acid and 2 ml of stannous bromide reagent. Transfer the mixture to a 25-ml volumetric flask, cool to room temperature, and dilute to the mark with water. Measure the absorbance against a reagent blank of the solution at 427 mμ and use to calculate the rhodium concentration of the sample.

5. Determination of Iridium (23, 17)

Reagent:

Stannous Chloride in Hydrobromic Acid, 5% - prepare by dissolving 12.5 g of $SnCl_2.2H_2O$ in 50 ml of redistilled concentrated hydrobromic acid with gentle warming. Cool the solution to room temperature and dilute to 100 ml with water. The solution should be prepared fresh daily and should be nearly colourless immediately after preparation.

Experience has shown that, to obtain a colourless reagent solution, only clear stannous chloride crystals that dissolve readily in hydrobromic acid should be used. Stannous chloride crystals that have a dull frosted appearance and are difficultly soluble in hydrobromic acid produce an intensely coloured solution that is unsuitable as a reagent for iridium.

Colour Development:

Transfer the hydrobromic acid solution of iridium from Section C.8 (d) or (e) to a 250-ml beaker and evaporate it to dryness in the presence of a few mg of sodium chloride. Add 7 ml of concentrated hydrobromic acid (which should not be coloured), cover the beaker with a watch-glass, and boil the solution until it has evaporated to 2.0 to 2.5 ml (as judged visually – using a blank for comparison, if necessary). Transfer the solution to a 25-ml volumetric flask by washing with 3-ml of concentrated hydrobromic acid and 7 ml of 25 per cent (v./v.) phosphoric acid. Place the flask in a boiling water bath and, after 10 minutes, add 5 ml of stannous chloride reagent. Exactly 2 minutes after reagent addition, remove the flask, and cool to room temperature in a cold water bath. Dilute the solution to the mark and measure the absorbance of the iridium complex at 402 mμ against a reagent blank.

6. Determination of Ruthenium (24)

Reagents:

p-nitrosodimethylaniline, 0.15% – prepare by mixing p-nitrosodimethylaniline with approximately 75 ml of water in a suitable flask, and heat in a water bath near the boiling point for approximately 30 minutes. Cool, filter the resulting solution through a fast paper, and dilute to 100 ml with water. The reagent solution is usually stable for several weeks, but should be replaced when there is evidence of a flocculent precipitate.

Buffer Solution, pH 4.1 – prepare by mixing 100 ml of 2 M sodium acetate solution (16.4 g/100 ml) with 100 ml of 8 M acetic acid (48 ml glacial acetic acid/100ml).

Colour Development

Evaporate the hydrobromic acid solution of ruthenium from Section C.5 (containing less than 30 μg of ruthenium) just to moist salts in a 250-ml beaker (the use of an air-jet is convenient to avoid overheating during the last stages of evaporation). Cool, add 1 ml of buffer solution

(pH 4.1) and 9 ml of water, and, using a pH meter, adjust the pH of the solution to the range 3.9 to 4.2 by the dropwise addition of a saturated solution of sodium bicarbonate. Transfer the solution to a 25-ml volumetric flask (without washing), add 2 ml of 0.15 per cent p-nitrosodimethylaniline solution, and heat at 70 ± 3°C in a water bath for 50 minutes to develop the colour. Measure the absorbance of the solution at 600 mμ against a reagent blank that has been simultaneously taken through the above procedure and, from this, determine the amount of ruthenium present.

7. Determination of Osmium (25)

Reagents:

Pyrogallol Solution, 2% – prepare by dissolving 2 g of reagent-grade pyrogallol in 100 ml of distilled water containing 2 to 3 drops of 12 N hydrochloric acid (to inhibit atmospheric oxidation). This reagent should be prepared fresh daily.

Buffer Solution, pH 2.2 — prepare as in C.8. above.

a) Colour Development:

Place the hydrobromic acid solution of osmium from C.1. above (containing up to 350 μg osmium) in a 250-ml beaker. Add 1 ml of a 2.5 per cent sodium chloride solution and evaporate the sample just to dryness. Dissolve the salts in 10 ml of water and then add 1 ml of buffer solution (pH 2.2) and 5 ml of 2 per cent pyrogallol solution. Using a pH meter, adjust the pH to 2.9 to 3.1 by the dropwise addition of a saturated solution of sodium bicarbonate. Transfer the sample solution to a 25-ml volumetric flask (without washing) and heat it in a boiling water bath for approximately 30 minutes. (The maximum colour develops within 10 to 15 minutes, but as a precaution the longer heating time is preferable.) Cool the flask to room temperature (in running water) and dilute the contents to volume with water. After mixing, allow the sample to stand for 15 minutes and then measure its absorbance at 585 mμ against either water or a reagent blank.

b) Extraction of Osmium-Pyrogallol Complex:

When less than 100 μg of osmium is to be determined, transfer the 25 ml of blue solution from (a) above, to a 60-ml separatory funnel and extract the osmium complex with two separate 5-ml portions of n-amyl alcohol. Combine the extracts and centrifuge for a short time to remove water droplets. Measure the absorbance against water or a reagent blank at 585 mμ, and from this determine the amount of osmium present.

Note:

Ruthenium interferes in the determination of osmium. Therefore, if the solution to be analyzed by the procedures given above was derived from a sample in which the ratio of ruthenium to osmium was high (e.g. greater than 100 to 1, as in a precious metals concentrate), it is recommended that the distillation of osmium as in C.1. be repeated to ensure that a complete separation of the two metals has been effected.

8. Determination of Gold (26)

Reagent:

o-Tolidine—to prepare, saturate 1 N sulfuric acid with reagent-grade o-tolidine, filter the saturated solution through a glass frit (do not use filter paper) and dilute the filtrate with 19 volumes of 1 N sulfuric acid.

Colour Development:

Evaporate the aqua-regia-containing gold solution from C.4. to approximately 1 ml by gently heating (a water bath at approximately 70°C), then take to dryness with the aid of a jet of compressed air while the warm beaker is swirled in the hand. (Care is required, during evaporation, to prevent thermal decomposition of chloro-aurate.)

Cool the beaker to room temperature, add 25 ml of o-tolidine reagent, swirl, allow to stand for a minute or two, transfer an aliquot of the yellow solution to a spectrophotometer cell, and read the absorbance at 440 mμ. The absorbance of the solution increases rapidly for the first 3-4 minutes, then becomes relatively constant after 7-10 minutes and remains so long enough for several samples to be handled simultaneously.

Note:

Although the o-tolidine method was satisfactory in the development of the proposed analytical scheme, a method of greater specificity may be more suitable when gold is to be determined routinely. It is suggested that the interested reader should consult the review by Beamish (27) for an assessment of other available spectrophotometric methods of gold.

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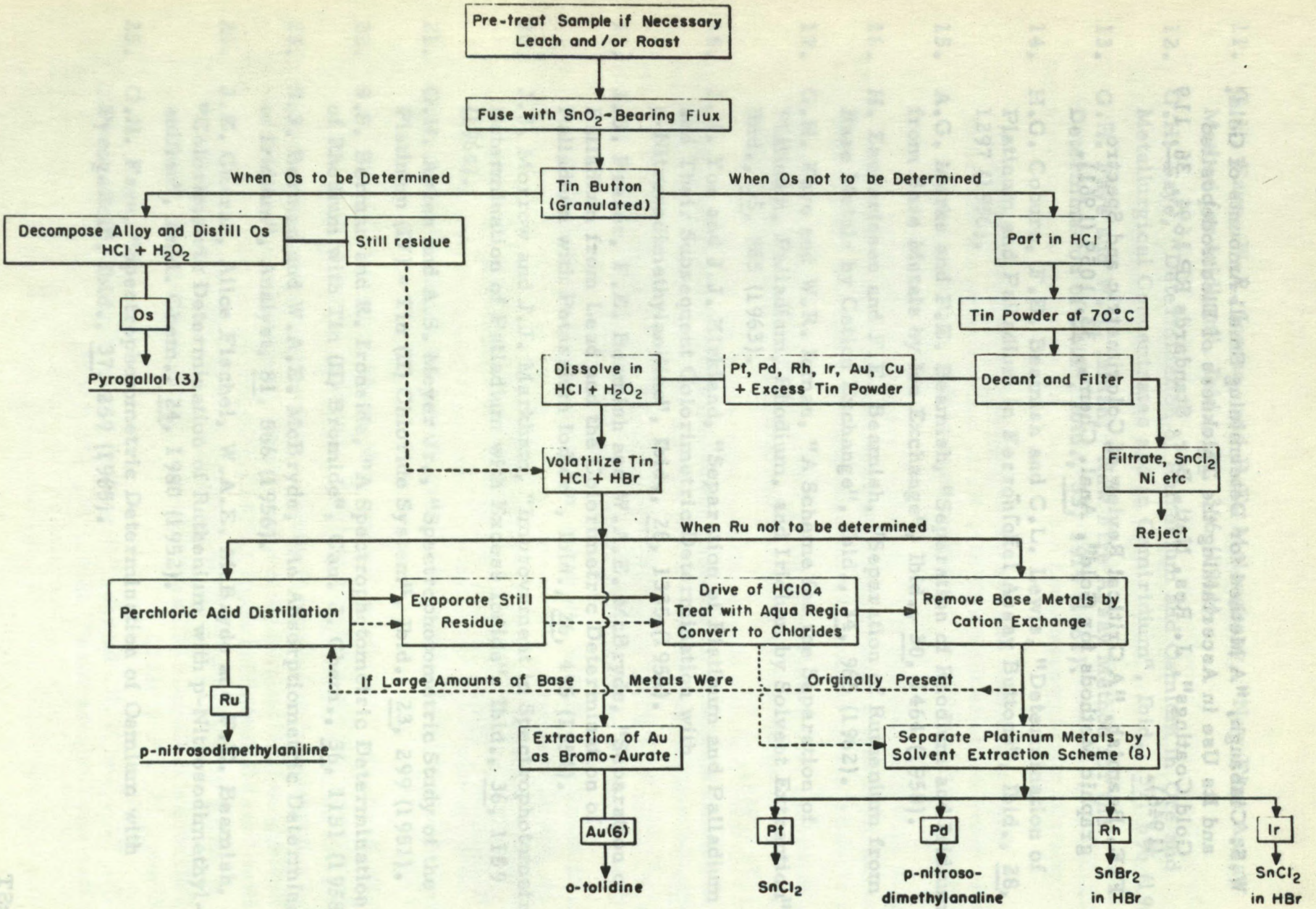

Figure 1. Flow sheet for new scheme of analysis for precious metal.

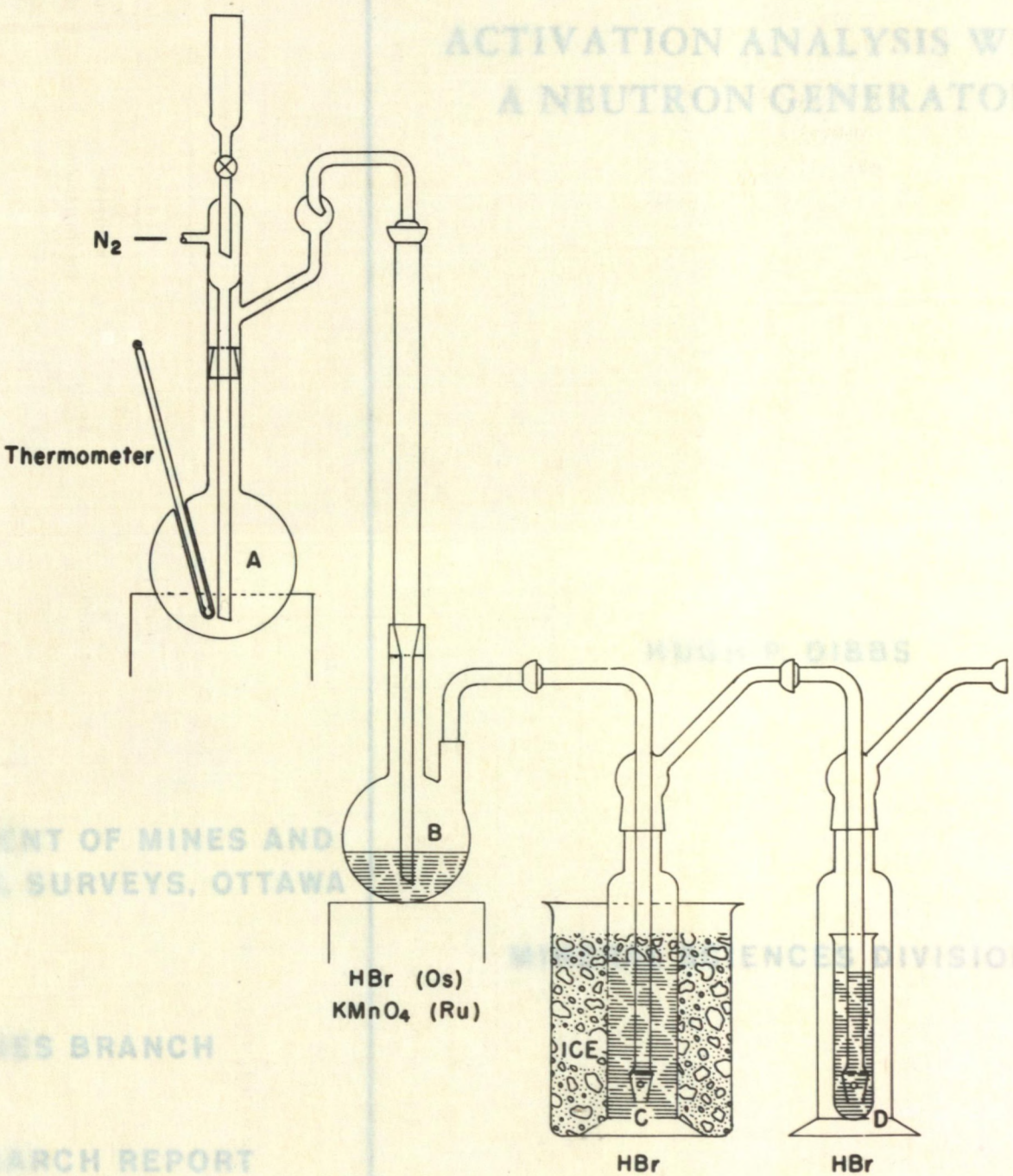

Figure 2. Distillation apparatus.