Fire Assay-Emission Spectrographic Determination of Iridium, Ruthenium, and Osmium

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A method is presented for the determination of microgram levels of Ir, Ru, and Os in ores, concentrates, and heavy sands. Radiotracers are used to monitor the recovery of these three metals in a 10-mg Pt bead during the normal fire assaying procedure. The Pt bead is arced at 20 A dc in a graphite electrode, and Pt serves as an internal standard. The precision of the method for Ir, Ru, and Os is about 5, 10, and 22% coefficient of variation, respectively. If high accuracy is not required, empirical correction factors may be applied for the assay losses of Ir and Ru, thereby eliminating the need for radiotracers.

INDEX HEADINGS: Analytical method; Fire assaying; Emission spectroscopy; Pt group metals.

INTRODUCTION

The Reno Metallurgy Research Center of the Bureau of Mines is providing analytical support for the Bureau's mineral resource and metallurgical research on ores and concentrates. With respect to the precious metals, the main effort is the fire assaying for gold and silver; however, there is an adjunct requirement for determining the platinum group metals. A previous report[1] by this Center described a rapid and reasonably accurate fire assay-spectrographic method for determining Pt, Pd, and Rh. In an extension of this work, a somewhat similar analytical scheme has been applied to the determination of Ir, Ru, and Os.

Numerous difficulties are encountered in the assaying of minerals, ores, and concentrates for Ir, Ru, and Os. Beamish[2] in his monograph pointed out that Ir does not alloy with Pb but is collected as a suspension in the metal. Nevertheless, a satisfactory assay can be made if the lead button is dissolved and analyzed chemically to avoid the mechanical losses that are often attendant to the normal cupellation process. Faye and co-workers[3] proposed the use of tin, instead of lead, coupled with acid dissolution and solvent extraction to recover the Ir. In chapter 6 of Beamish's monograph,[2] Lewis has summarized the various fire assay-spectrographic methods for the Pt group metals, and he concluded that one of the unsolved problems is the determination of Ir, Ru, and Os in fire assay beads. Schnepfe and Grimaldi[4] found that Ir, at the 2.5 ppm level or greater, could be recovered quantitatively in a gold bead and subsequently dissolved and determined by atomic absorption.

Thiers, Graydon, and Beamish[5] used radiotracer techniques to show that, even under idealized conditions, serious losses of milligram amounts of Ru occur during the classical fire assay. They reported that the major loss of Ru occurs in the cupellation and is not due to volatilization, but rather to absorption into the cupel. Allan and Beamish[6] studied the behavior of milligram quantities of Os during fire assay with lead as a collector. They reported that, despite carefully controlled conditions, considerable loss of Os can occur during the fusion, and that the cupellation of lead buttons is inadmissible, because the Os is readily volatilized as the tetroxide. Faye[7] reported that both Ru and Os could be collected in tin and analyzed by chemical procedures. Inman[8] has presented a complete analytical scheme for the precious metals that appears to be efficient but also very time-consuming.

In the present study, radiotracers were used to monitor the fire assay recovery of Ir, Ru, and Os under various conditions. The results led to a fire assay-spectrographic procedure which was reasonably fast and reliable for all three elements.

I. EXPERIMENTAL METHOD

A. Equipment and Radioisotopes

In addition to the standard fire assay equipment, a Jarrell-Ash[9] 3.4-m, wide angle Wadsworth-mount emission spectrograph, equipped with a 30,000-line/in. grating and a 30-in. plateholder, was used in conjunction with a source unit capable of producing dc arcs of up to 30 A. Light attenuation at the spectrograph slit was provided by a rotating, adjustable two-step sector.

A themostatically controlled photoprocessor was used for developing plates, and spectral lines were measured on a microphotometer. Transmittance values were converted to intensity ratios by means of a drum-type calculating board.

Gamma ray counting of the radiotracers was accomplished with a 3- × 3-in. NaI (Tl) well-type crystal coupled through a photomultiplier tube to a RIDL-34B multichannel analyzer and accessory readout equipment.

The elements studied have radioisotopes which have relatively long half-lives and decay with gamma ray emissions. The gamma rays associated with the ruthenium isotope actually arise from the decay of the 30-sec half-lived daughter, ^{106}Rh. This presents no problem in counting because radioisotopic equilibrium is reestab-

TABLE I. Properties of radioisotopes.

Isotope	Half-life (days)[10]	Principal gamma rays (keV)[10]
^{192}Ir	74.2	296-612 (complex)
^{106}Ru	368	512 622
^{185}Os	93.6	646 875

lished within a few minutes after any separation of the mother and daughter isotopes. The half-lives and principal gamma ray energies of the radioisotopes used are presented in Table I.

All of the isotopes were obtained commercially as chloro complexes in HCl solution and were utilized in that chemical form. The Ru and Os were purchased from Amersham Searle Corporation and the Ir from the Oak Ridge National Laboratory. Prior to actual use, the tracers were diluted to the desired concentration with 1 *N* HCl. With Ru and Ir, 0.2 μg/ml of the respective metals were also added to serve as carriers to prevent selective adsorption of the tracer on the container walls. This was not required with Os, because sufficient carrier was present in the solution as received. No particular efforts were required to establish the same chemical species of the tracer ions in solution and the elements being tagged, because this was accomplished in the actual fire assay step.

Os, Ir, and Ru are not readily soluble in acids or mixed acids, and so these metals were dissolved by a KOH-KNO_3 fusion. In the case of Ru, Na_2O_2 was also required in the fusion mix. The Ru and Ir melts were dissolved in HCl, evaporated to near dryness, and diluted to volume with 1 *N* HCl. The Os solutions were unstable in acid media when in plastic bottles; therefore, the Os melt was dissolved in 1 *N* NaOH. Aliquots of these master solutions were then diluted as required. Carrier solutions of Pt, Pd, and Au were prepared by dissolving the appropriate amount of the metal in aqua regia, evaporating to near dryness, and diluting the solution to the proper volume with 1 *N* HCl. Ag carrier was similarly prepared in HNO_3 solution.

B. Fire Assay

The fire assay procedure, which was originally developed for the analysis of gold- and silver-bearing ores,[11] was an ancient and time-honored art even in Agricola's time. Under proper conditions, it can also be applied to the collection of the platinum group metals. In general, the procedure involves the addition of fluxing materials to the ore or sample, which normally forms a readily fusible homogeneous slag when heated. Concurrent with the slag formation, a collecting or alloying metal, usually lead, is produced *in situ* by reduction of part of the flux mixture. The noble metals are simultaneously reduced from the ore and are collected by the droplets and mist of falling lead that form a pool at the bottom of the slag. The molten mix is poured into an iron mold, and, after cooling, the lead button is separated from the slag and treated by a process

TABLE II. Spectrographic condition.

Sample:	10-mg Pt bead.
Spectrograph:	Jarrell-Ash 3.4-m, Wadsworth mount, 30 000 grooves/in. grating.
Electrodes:	Anode: ⅛-in.-diameter graphite with ¼-in.-deep cup, Ultra Carbon 5440. Cathode: ⅛-in.-diameter graphite ASTM shape C-1, Ultra Carbon 1992.
Excitation:	dc arc burning at 20 A (with shorted electrodes).
Arc gap:	4 mm, maintained during burn.
Exposure:	40 sec.
Wavelength range:	2400–3600 Å, first order, 30 000-line/in. grating.
Spectrograph slit:	10 μ wide, 1.8 mm long.
Attenuation:	5% and 25% transmittance, 2-step sector at slit, 100-mesh wire screen at arc stand.
Emulsion:	Kodak SA No. 1.
Processing:	Kodak D-19 developer, 5 min; Kodak indicator stop bath, 20–30 sec; Kodak rapid fixer with hardener, 4 min; wash, 10–20 min; dry with forced warm air.

TABLE III. Spectral lines and concentration ranges.

Element	Analytical line (Å)	Range (μg)
Ir	2849.73[a, b]	0.5–50
Os	2637.13[b]	0.5–50
Ru	2916.26[a]	10–50
	2874.98[b]	0.25–10
Pd	2922.49[a]	10–100
	3242.70[a]	0.25–10
Rh	3372.25[a]	2.5–50
	3323.09[a]	0.25–5

[a] Measured at 5% transmission, Pt internal standard line 2744.83 Å.
[b] Measured at 25% transmission, Pt internal standard line 2744.83 Å.

called cupellation. This separates the lead from the precious metals, which form a bead called a prill. Bugbee[12] and Beamish[2] have written comprehensive discussions on fire assaying.

Test samples were prepared for fire assay by pipetting the proper amount of the Ir, Ru, and Os solutions, plus the corresponding tracers and the carrier metal solutions, directly onto blank charges in the assay crucibles. Precautions were taken to ensure that the solutions were adsorbed by the assay mix and not the walls of the crucibles. The solutions were allowed to dry overnight, and the charges were thoroughly mixed, fused for 45 min at 1050°C, and poured into conical molds. The lead buttons obtained were then cupelled at 860°C. The resulting tagged beads were weighed and placed in test tubes, and the gamma ray activity was counted. These activities were compared to the activities of standard solutions of the tracers to determine the percentage recovery of each of the metals. Only small corrections were required to compensate for the differences in self-absorption of the emitted gamma rays between the metal beads and the standard solutions.

C. Spectrographic Procedure

Spectrographic standards were prepared as previously described using platinum as carrier. The standard charges were then assayed, and the beads were counted for their contained radioactive isotopes. The percentage of recovery was determined by comparison to a standard tracer, and the amount of the recovered metal was calculated. These beads were then arced at the conditions listed in Table II. Quadruplicate standards were made for each metal concentration. To extend the usefulness of the technique, standards were prepared containing palladium and rhodium.

The spectral lines used and their corresponding concentration ranges are shown in Table III. Analytical curves were determined from intensity ratios by a regression analysis program. Emulsion calibration was implemented by a two-step preliminary curve method.

II. RESULTS AND DISCUSSION

A. Fire Assay

Initially, several different potential carrier metals were evaluated for their ability to act as collectors for these particular platinum group metals. The use of Pt, Pd, Au, and Ag was investigated with tagged Os, Ir, and Ru.

The assessment of the carrying efficiency of 10 mg of various metals, for 20 μg of Os, Ir, and Ru, is presented in Table IV. Because platinum was obviously the best choice, further evaluation of the other potential carriers for low microgram levels of Ru and Os was unnecessary. Initially, 10 mg was chosen arbitrarily for the carrier weight, because it produced convenient size beads that were easy to handle both in assay and in subsequent analysis. A smaller bead is readily lost and is easily ejected from the electrode. Larger beads are more dilute with respect to the elements being analyzed, and the extra Pt only adds to the spectral background.

Recovery of the Pt, which also served as the internal standard during the spectrographic analysis, was established by reassaying the slag from the fusion and by grinding and assaying the cupels. The carrier metals were collected in 10-mg silver beads, which were then spectrographically analyzed by Whitehead's method.[1] Only about 0.2% of the added Pt was in the slag and 0.6% in the cupels. This agreed with atomic absorption determination of the Pt in the beads. Less than 1% of the Pt carrier is lost in the fire assay procedure; therefore, practically no error would result from the use of Pt as an internal standard for the spectrographic analysis.

TABLE IV. Comparison of four carrier metals.

Carrier metal	Recovery (%)[a]		
	Ir	Ru	Os
Ag	86	7	3
Au	88	24	26
Pd	88	14	47
Pt	99	63	54

[a] Recovery based on 20-μg amount of metal added.

TABLE V. Recovery of Ir, Ru, and Os, in the platinum bead, in two different assay fluxes.

Type of flux	Metal added (μg)	Recovery (%)		
		Ir	Ru	Os
Slightly acid	200	77	97	78
	100	80	69	67
	20	99	63	54
	1	90	52	15[a]
Basic	20	93	75	56
	1	93	59	11[a]

[a] The amount of Os added was 5 μg.

Two separate flux mixes were investigated, one of which results in a slightly acid slag and the other of which gives a basic slag. The acid flux, which is used with silicious ores, results in a slag having about 40 equivalent mole % silica with a composition between a monosilicate and bisilicate. This mix contains 65 g of PbO, 24 g of Na_2CO_3, 10 g of SiO_2, 10 g of $NaB_4O_7 \cdot 10\ H_2O$ (borax), and 2.5 g of regular kitchen flour. The highly basic flux produces a subsilicate slag containing the equivalent of 20 mole % silica and is used with ores containing copper. This particular flux, which contains 125 g of PbO, 20 g of Na_2CO_3, 10 g of SiO_2, and 2.5 g of flour, was investigated because platinum group metals are often associated with copper-nickel ores.

Recovery of Ir, Ru, and Os in the platinum bead, using the two types of flux, is presented in Table V. These data, representing six determinations, show that the collection of the three elements is independent of the nature of the flux within the limits tested. Also, the recovery of the individual metals is not particularly dependent upon the amount of the metal present except for Os, which is extremely dependent at low concentrations. Ir exhibits somewhat higher losses when present in greater than 50-μg quantities. If relatively large amounts of Ir are encountered in a sample, a more quantitative recovery may be accomplished by reducing the sample size or by adding greater amounts of Pt. This, however, would require the restandardization of the method.

Experiments were conducted to determine if precious metals were lost during the fusion process. Assay charges were prepared, as previously described, and the tagged lead buttons were recovered. Standards were prepared by pipetting the same solutions into lead foil boats and carefully evaporating the solutions to dryness. The boats were then folded, and lead foil was added to equal the weight of the lead buttons. Both samples and standards were formed into uniform-sized 1-mm-thick discs by using a hydraulic press and mechanical rolls. The radioactivity in the lead discs was counted, and the count rate of the samples was compared to the count rate of the standards. To determine the homogeneity of the tracers in the lead, the discs were cut into small pieces which were then individually weighed and counted. The activities were compared on a counts per unit weight basis. In addition to this method, autoradiograms were made of the lead buttons. Special buttons were prepared containing

TABLE VI. Recovery of Ir, Os, and Ru in lead buttons.

Element	Metal added (μg)	Recovery (%)	Coefficient of variation (%)
Ir	20	99.6	0.6
Os	20	92.1	14.9
Ru	20	97.8	0.7

about 10 times the usual activity. The lead was carefully cleaned of any adhering slag and sliced vertically, and the sections were polished. These sections were placed on autoradiographic plates for an appropriate length of time, and the exposed plates were developed by normal established procedures.

The collection of Os, Ir, and Ru in the lead buttons is shown in Table VI. The recoveries of both Ir and Ru are nearly quantitative and very reproducible. However, the Os results showed poor reproducibility and were not quantitative. The reason for this behavior became quite evident after rolling the lead into a 1-mm sheet, sectioning it, and counting the segments. The Os activity showed an extremely heterogeneous distribution throughout the lead. Several buttons were then carefully sectioned so that the position of the individual pieces could be determined. These pieces, when counted, showed that the greatest activity was sometimes at the apex of the cone and sometimes at the top surface or edge of the cone.

Autoradiographs of vertically sectioned lead buttons confirmed this finding. Therefore, small mechanical losses of the Os in the lead buttons could easily account for the lack of precision. Both the counting of the individual lead pieces and the autoradiographs showed that the Ir and Ru were quite homogeneously distributed throughout the button. Although this appears to contradict Beamish,[2] it must be remembered that the amount of Ir in this study was only 20 μg, whereas Beamish was discussing macro quantities.

Because Ru and Os can form volatile tetroxides readily, the use of high temperatures during cupellation is prohibited. Attempts were made, therefore, to determine the minimum temperature at which cupellation would proceed to completion. Furnace temperatures were measured directly over the surface of the lead in the cupels, and a special inner furnace was constructed of fire brick to reduce the temperature fluctuations associated with an electric assay furnace. During the initial stage of cupellation, the temperature of the furnace is normally high, about 930°C, so that the litharge resulting from the oxidation of the lead melts readily and is adsorbed by the cupel. When this opening phase proceeds steadily, the temperature of the furnace can be lowered, because the heat of oxidation raises the temperature of the lead above that of the furnace. Attempts were made to reduce this initial high furnace temperature by "opening" the lead with a carbon monoxide lance. Experiments with the CO lance, while successful in lowering the "opening" temperature, indicated that the crucial time during the cupellation appears to be just prior to the freezing of the Pt bead. Consequently, the use of the lance was ineffective.

TABLE VII. Effect of cupellation temperature.

Cupellation temperature (°C)	Metal added (μg)	Recovery (%)	
		Ru	Os
Open 930, finish 930	5	49	2
	25	62	41
Open 930, finish 860	5	52	15
	25	67	54

The temperature at which cupellation was carried out had no effect on the recovery of Ir, and only a slight effect on Ru. However, variations in temperature grossly affected the recovery of Os, as shown in Table VII. Several attempts to control carefully the temperature of the lead button in its final stage of cupellation proved to be futile, and the use of the inner furnace liner was discontinued. While an electric assay furnace may be reasonably well controlled, the actual variation in cupel temperature during an "on-off" cycle may be considerable, owing to the radiant heating from the furnace elements. When determining low-microgram levels of Os, it is extremely difficult, if not impossible, to duplicate recoveries even when the samples are side by side during cupellation. Temperatures below 930°C required unduly long opening times, and a finishing temperature much below 860°C caused premature freezing of the lead with subsequent loss of the sample. Consequently, as a standard practice, the buttons were opened at 930°C, and then the furnace temperature was allowed to drop to 860°C for finishing.

B. Spectrographic

In the previously described fire assay-spectrographic procedure,[1] the Pt, Pd, and Rh were collected in a 10-mg Ag bead, and 10 mg of Pt or Rh metal powder were added to the electrode to serve as a buffer and internal standard. In the present method, the 10-mg Pt beads containing Ir, Ru, and Os are arced directly without the use of any additives. The Pt beads burn very smoothly, with no tendency to be ejected from the electrode, and the Pt serves as an internal standard for other metals.

Jumping plate studies were conducted to determine the behavior of Ir, Ru, and Os with respect to Pt. The sample used for this purpose was a mixture of metal powders containing 1 mg each of Ir, Ru, and Os, and 10 mg of Pt. Previous work had established that Pt beads and Pt metal powders behave similarly in the arc. Using a 10-A dc arc in conjunction with a 5440 electrode, most of the Pt vaporized long before the Ir, Ru, and Os, and a burn time of about 90 to 100 sec was required, as shown in Fig. 1. When the arc current was increased to 20 A the distillation behavior of Ir, Ru, and Os closely approximated that of the Pt, and the burn time was reduced to 40 to 50 sec (Fig. 2). A comparison of these data shows the marked improvement that was achieved by increasing the current from 10 to 20 A.

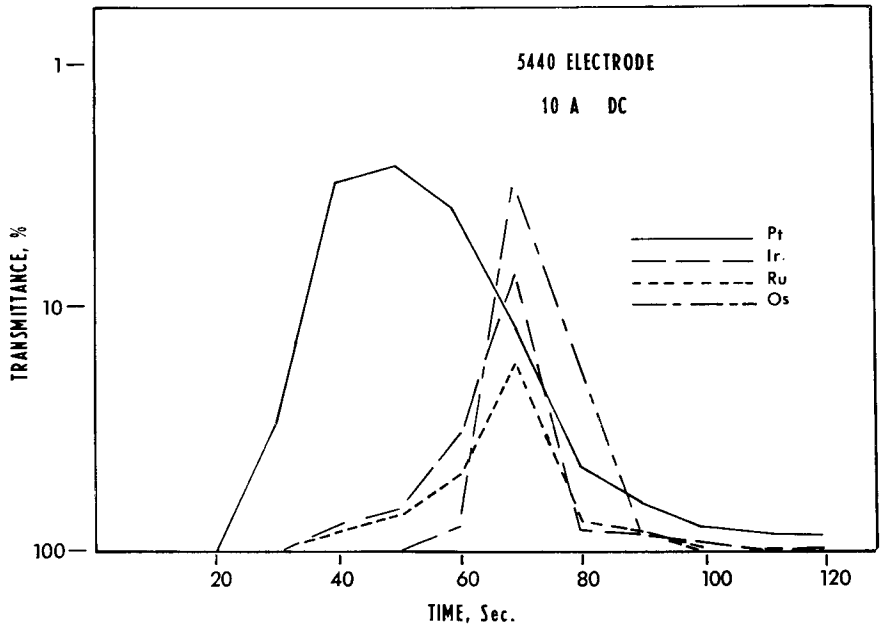

FIG. 1. Distillation behavior of Pt, Ir, Ru, and Os in 5440 electrode at 10 A dc.

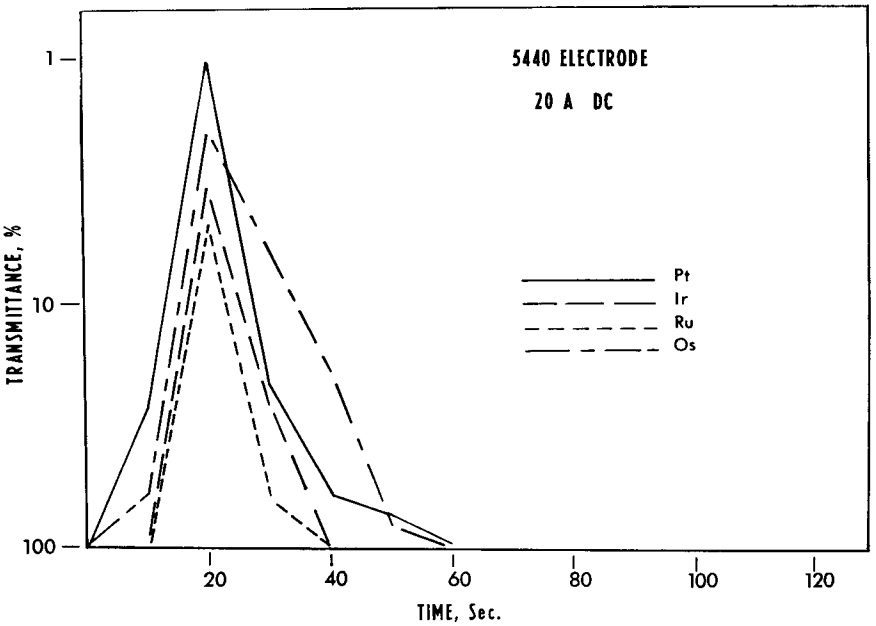

FIG. 2. Distillation behavior of Pt, Ir, Ru, and Os in 5440 electrode at 20 A dc.

In another jumping plate study, a comparison was made between the thin-walled, deep, 5440 electrode and the thick-walled, shallow, 105-S electrode. The Pt beads were arced at 20 A in the 105-S electrode, and the resulting distillation behavior of Ir, Ru, and Os with respect to Pt is shown in Fig. 3. A comparison of Figs. 2 and 3 shows that the 5440 electrode afforded the preferred distillation pattern, and the total burn was completed in a much shorter time. Accordingly, all of the subsequent Pt bead standards and samples were arced at 20 A for 40 sec in the 5440 electrodes.

C. Precision and Accuracy

The over-all precision of the radiotracer procedure involving the pipetting of the solutions and counting of the samples is less than 2% coefficient of variation The coefficient of variation of counting the individua platinum beads in repetitive determinations for either Ir or Ru is in the 1 to 2% range. Therefore, the principal source of nonreproducibility can be attributed to the optical spectrographic step.

Precision and accuracy were checked further by analyzing synthetic samples which had been prepared by the procedure described for the Pt bead standards. Each sample was analyzed in triplicate on two different days, and the results are shown in Table VIII. However, as might be expected, the precision is somewhat poorer with actual ore samples. Owing to the heterogeneous distributions of the platinum group metals and the extremely small amounts encountered in naturally

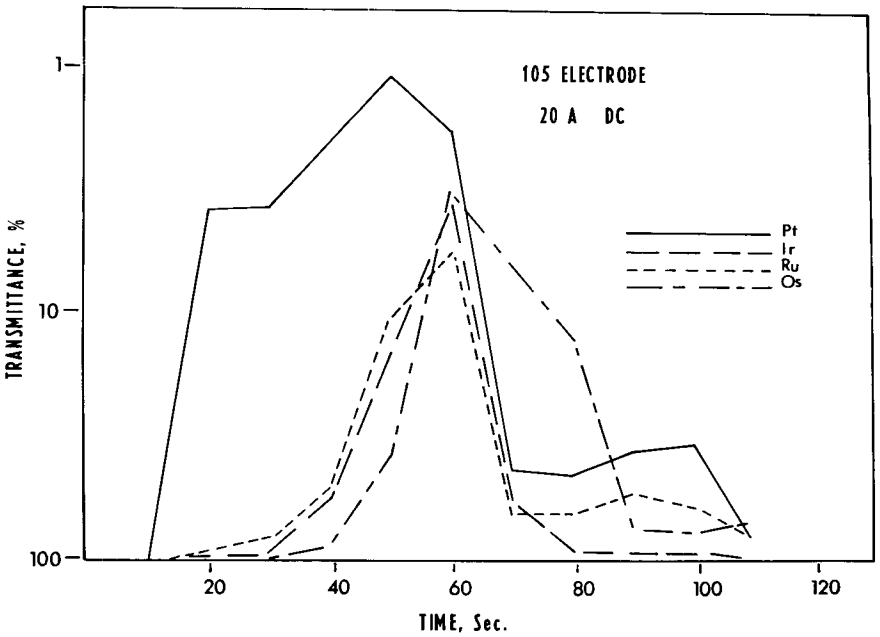

FIG. 3. Distillation behavior of Pt, Ir, Ru, and Os in 105-S electrode at 10 A dc.

TABLE VIII. Analysis of synthetic samples.

Element	Known (μg)	Found (μg)	Coefficient of variation (%)
Ir	10.0	9.9	6.0
	40.0	38.5	4.0
Ru	10.0	10.0	13.0
	40.0	40.4	7.9
Os	10.0	8.5	20.0
	40.0	34.5	23.8

TABLE IX. Analysis of ores and concentrates.

Sample	Sample size (g)	Found (ppm)			Coefficient of variation (%)		
		Ir	Ru	Os	Ir	Ru	Os
Rustenburg Pt ore (South Africa)	15–120	0.14	0.61	0.11	8.1	15.0	9.3
Placer concentrates (Yuba River, Calif.)	7.5–15	1.5	1.1	3.7	5.5	28.1	14.8
Cu-Ni concentrate (Sudbury, Canada)	7.5	0.35	0.75	[a]	8.2	9.7	
Cu-Ni matte (Sudbury, Canada)	7.5	0.62	1.1	[a]	2.1	9.4	
Placer concentrate (Colombia, South America)	7.5	2.4	0.06	2.6	6.6	9.9	26.2

[a] Not detected.

occurring materials, it is very difficult to obtain representative samples of ores and physical concentrates. Furthermore, it is extremely difficult to obtain a good fusion on highly metallic samples such as Cu-Ni mattes and certain heavy sand concentrates. Therefore, one must reach a compromise between the desired sample size and the amount that can be handled in a fusion. The data presented in Table IX represent four different and divergent types of materials: platinum ore, black sands or placer concentrates, Cu-Ni concentrates, and a Cu-Ni matte. These samples were each analyzed

TABLE X. Determination of Pd and Rh in ores and concentrates.

Sample	Sample size (g)	Found (ppm)		Accepted value (ppm)	
		Pd	Rh	Pd	Rh
Rustenburg Pt ore (South Africa)	15–120	1.9 ± .3[a]	0.29 ± .03	2.1 ± .1	0.34 ± .06
Cu-Ni matte (Sudbury, Canada)	7.5	7.9 ± 1.2	0.99 ± .14	7.9 ± .4	0.93 ± .11

[a] Standard deviation.

in triplicate on 2 separate days by the described procedure. It would have been desirable to compare results on known samples, but to our knowledge independently analyzed or standard platinum group ore samples are not available.

One rather noteworthy observation was made at the conclusion of these 30 analyses. Despite the diverse nature of the samples and the fluxes required for proper fusion, both the Ir and the Ru recoveries were extremely constant. The Ir and Ru recoveries averaged 91.8 ± 6.8% and 59.6 ± 7.1%, respectively, as determined from the radioactive tracers. Consequently, if radiotracers are not available, these two values may be used to correct the spectrographic results for assay losses in materials of this type.

The spectrographic detection limit was less than 0.5 μg for Ir, Ru, and Os. Based on a 1-assay-ton sample, this limit would be about 15 ppb. The analytical range of the method can be varied by simply changing the size of the sample used in the fire assay, provided proper fusion of the sample can be accomplished. For example, a 4-assay-ton sample of the Rustenburg platinum ore was assayed for Os. After correcting for the 5 μg of Os that were added with the radiotracer, a net 13.0 μg (0.11 ppm) of Os were recovered. The analysis

range is not limited at the upper end; however, from the results described previously (Table V), the size of the sample would have to be decreased.

The determination of Pd and Rh was not included in this work because fire assay procedures for their recovery have been well documented.[1,2] However, to complement the use of this method, the determination of Pd and Rh in two separate samples is presented in Table X. These particular divergent samples were chosen because interlaboratory "round robin" analyses were available. The operating conditions for these analyses are the same as those described for Os, Ir, and Ru. The table shows that this method is also suitable for the reasonably accurate determination of these two additional platinum group elements.

In summary, a fire assay-spectrographic method has been developed for the rapid, sensitive analysis of precious metal-bearing materials for Ir, Ru, and Os. The use of radiotracers is essential to monitor the assay recoveries if maximum accuracy is required. Because of the consistency of Ir and Ru recoveries in usual platinum group metal samples, the values 90% and 60%, respectively, may be used to correct the spectrographic results empirically for fire assay losses. As the losses encountered with Os are extremely variable, an Os tracer is always required. The method is particularly suitable for surveying ores and placer concentrates for all of the noble metals except platinum.

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The Determination of Potassium in Graphite by X-ray Fluorescence Spectrometry

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A spectrochemical method has been developed for the determination of potassium in graphite covering the concentration range between 0.1 and 10%. After wet combustion of about a 100-mg sample, potassium could be analyzed by x-ray fluorescence spectrometry with a standard deviation <1% (rel.).

INDEX HEADINGS: X-ray fluorescence; Analytical method; Graphite crystal.

INTRODUCTION

In the course of a study of the mechanism of the penetration of potassium into the graphite lattice[1] a method has been developed for the determination of potassium in graphite by x-ray fluorescence spectrometry. The concentration range of about 0.1 to 10% K would be covered.

In principle the potassium content can be determined indirectly in such a binary system by a carbon determination using a classical combustion device for organic elemental analysis.[2,3] The special treatment of the sample necessitated by the reactivity of the substance excluded the indirect method, so that a direct wet chemical or spectrometric method had to be developed. Since x-ray fluorescence methods are very selective, precise, and versatile, this method has been preferred over atomic absorption owing to its higher precision and over wet chemistry owing to its simplicity.

I. EXPERIMENTAL METHOD

A. Sample Preparation

Adequate solid standards would make the problem very easy by using pellets from very fine powdered material after the transformation of the potassium into a stable compound (e.g., carbonate); since such standards are not available the sample has to be transferred into the liquid state. It will be shown that the loss of

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