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Fire-Assay Emission Spectrographic Method for Platinum, Palladium, Rhodium, and Gold

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A method has been developed for the determination of microgram levels of Pt, Pd, Rh, and Au. A 10-mg Ag bead containing the precious metals, as extracted by fire assaying, is arced at 8 A dc in graphite electrodes in the presence of 10 mg of either Rh or Pt metal powder. The matrix elements, Ag and Pt, or Rh, serve as internal standards, and intensity ratios Pt/Rh or Rh/Pt, Pd/Rh, and Au/Ag are determined. Precision of the method is about ±5% coefficient of variation for Pt and Rh, ±15% for Pd, and ±19% for Au. Limits of detection are below 1 μg, giving analysis limits (for a 1-assay-ton sample) of about 1–30 ppb for these precious metals.

INDEX HEADINGS: Analytical method; Emission spectroscopy; Noble metals.

INTRODUCTION

Under the Bureau of Mines Heavy Metals Program, the Reno Metallurgy Research Center has been providing analytical support for mineral resource and mining research work in the Western United States. Initial analytical requirements were largely restricted to the fire assay of thousands of samples for Au and Ag. Later requirements necessitated development of a rapid, simple method for surveying many of the samples for possible Pt and Pd content.

Of first consideration in developing such a method is the concentration at which precious metals are encountered. The extremely low levels at which these elements occur in nature preclude their determination directly in the sample, and any technique for the measurement of these elements must be prefaced by some method of concentration. The fire assay is a logical choice for this purpose for two reasons: First, analytical recovery of the precious metals from ores and metallurgical products has been thoroughly studied and shown to be suitably efficient[1,2]; second, assay techniques have been carefully worked out and are already in routine use on the materials in question.

Concentration level, as it developed, was also the prime factor in choosing the analytical technique to be used once the metals of interest were collected. Even though a fire assay resulting in a 10-mg Ag doré from a 1-assay-ton sample provides concentration by a factor of 3000, the metals are likely to be present in the concentrate at very low levels. For this laboratory, the choice of technique suitable for low-level analysis lay between atomic absorption spectrophotometry and optical emission spectrography. Because a rapid, simple technique capable of handling a large number of samples was desired, the spectrographic approach was selected, thus avoiding the sample handling time required to prepare suitable solutions for atomic absorption.

A survey of the spectrochemical literature revealed that the most successful methods for fire-assay spectrographic analysis were those which used spark excitation of the fire-assay bead fastened to some type of electrode. Some of the techniques used include duplicate doré beads soldered to brass wires and used as an electrode pair[3]; doré beads supported in Ag funnels[4]; doré beads mounted on the point of a Cu rod[5]; Pb beads, formed by dissolving the doré bead in molten Pb,[6] or by stopping the cupellation before the Pb is completely removed,[7] mounted on flat-ended copper rods; and doré beads dissolved in aqua regia, with a portion of the solution dried on graphite electrodes.[8]

The lead bead method and the solution method appeared to be the most reliable, but neither was simple enough to serve as a rapid survey method. In addition, the arrested cupellation lead bead technique, requiring nonroutine participation of the fire-assay staff, would seriously affect the normal output of the fire-assay laboratory.

It appeared that the simplest, least disruptive procedure would be to arc doré beads in cupped graphite electrodes. Accordingly, a study of the variables involved in such a technique was undertaken, and the method herein described was established. Although the original need was for a rapid method of surveying large numbers of samples for Pt and Pd, the studies resulted in a method capable of good quantitative analysis for Pt, Pd, and Rh. In addition, Au may be determined, if needed, as a backup to fire assay. Because the fire-assay techniques used were quite standard,[2] they will not be described in this paper. The only nonstandard practice was the addition of 10 mg of Ag as collector rather than the more usual 2-mg inquart. The extra Ag provides a doré bead having a higher capacity for the collected metals, resulting in a method of wide concentration range.

I. EXPERIMENTAL WORK

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 accomplished by a rotating, adjustable two-step sector.

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

A. Preparation of Standards

The appropriate weight of high-purity Pt or Pd was dissolved in an excess of aqua regia. The solution was evaporated to near dryness and cooled, and aqua regia was added in an amount that would give 5% by volume in the finished solution. After the solids were dissolved, the solution was transferred to a volumetric flask and diluted to mark with pure H_2O. Subsequent dilutions were made by standard volumetric techniques wherein the acid concentration was maintained at 5% in each solution. Five solutions were thus prepared containing 1000, 100, 10, 1, and 0.1 μg/ml.

High-purity Rh powder was dissolved in hot concentrated H_2SO_4. The Rh was only slowly soluble in a large excess of acid at fuming temperatures. When the Rh was completely in solution, the acid volume was reduced by evaporation to an amount which would be 10% by volume in the finished solution, cooled, transferred to a volumetric flask, and diluted carefully with H_2O. Final dilution to mark was delayed until the flask and its contents had cooled. Because of solubility problems, only enough Rh could be kept in solution during the evaporation to prepare 200-μg/ml stock solution. Subsequent dilutions were made, keeping the acid concentration constant, to give solutions of 100, 10, 1, and 0.1 μg/ml.

High-purity Au was dissolved in aqua regia, evaporated to dryness, and made basic by the addition of a few drops of NH_4OH. The residue was dissolved in aqueous NaCN, transferred to a volumetric flask, and diluted to mark with H_2O. Subsequent dilutions were made as for the other metals, with the NaCN content being maintained at 0.06%.

Standards were prepared by slowly evaporating various amounts of the solutions in boats fashioned from about 2 g of Pb foil. The boats were then placed into fire-clay crucibles, flux and Ag were added, and the standard fire-assay treatment was carried out. One set of standards contained Pt, Pd, and Au, and another contained Rh, Pd, and Au. Six standards were prepared for each concentration, the elements being arranged so that standards containing high levels of one element had low levels of the others. Thus, the total element content (exclusive of Ag) was kept at or below about 2 mg. A summary of the content of the resulting Ag bead standards is shown in Table I.

The standard beads were arced at the conditions listed in Table II. Electrodes were loaded by placing a bead in the cup and adding the weighed amount of the proper buffer. The first standard set was run as three sets of duplicates. The second set, containing Rh, was arced similarly, except that Pt was used as the buffer.

Table I. Composition of standard beads.

	Amount of element, μg		
Standard No.	Pt (or Rh)[a]	Pd	Au
1	2000	0	0.05
2	1000	0.05	0.2
3	500	0.1	1
4	200	0.2	5
5	100	0.5	20
6	50	1	100
7	20	2	500
8	10	5	2000
9	5	10	1000
10	2	20	200
11	1	50	50
12	0.5	100	10
13	0.2	200	2
14	0.1	500	0.5
15	0.05	1000	0.1
16	0	2000	0

[a] Pt for first set, Rh for second set.

The spectral lines used and their corresponding concentration ranges are given in Table III. Except as noted, all lines were measured in the light step, and background corrections were made where indicated. Working curves were constructed from intensity ratio–concentration relationships, as standard spectrochemical practice. Emulsion calibration was by a computer-assisted two-step preliminary curve method.

B. Analysis of Samples

Samples are normally submitted to the fire-assay laboratory with instructions to prepare a 10-mg Ag bead for spectrographic analysis. If both Pt and Rh are to be determined, two beads are prepared. The Ag beads are loaded into electrodes with the proper buffer and arced as previously described. Spectral lines are measured, intensity ratios are calculated, and amounts of the elements in the bead are read from the working curves. The weight of an element can be converted to ounces per ton according to

$$C = w/1000f, \qquad (1)$$

where C is the concentration of element in original sample in oz/ton, w the weight in micrograms of element found, and f the fraction or multiple of a 1-assay-ton sample used. If f is not known to the spectrographic laboratory staff, the analyst reports the weights of the precious metals found in either micrograms or milligrams, depending on the magnitude of the number.

II. RESULTS AND DISCUSSION

Some difficulty in arcing Ag beads in graphite electrodes was encountered initially owing to the use of high arc currents to provide good vaporization rates for refractory Pt. Good spectral intensity over suitably short exposure was obtained, but the precision was poor, apparently because of sample ejection resulting from violent boiling of molten Ag. Lower arc currents (5 A) prevented sample ejection, but refractory Pt was not vaporized until Ag had been depleted, several minutes into the burn and then only slowly. Switching to high current prior to Ag depletion resulted in ejection.

Table II. Spectrographic conditions.

Sample:	10-mg Ag doré bead plus 10 mg buffer. (Pt powder added for determination of Rh; Rh powder added for determination of Pt, Pd, and Au.)
Electrodes:	Anode: $\frac{1}{8}$-in.-diam graphite with $\frac{1}{4}$-in.-deep cup, Ultra Carbon 5440. Cathode: $\frac{1}{8}$-in.-diam graphite with rounded point, Ultra Carbon 5001.
Excitation:	Direct-current arc burning at ~8 A (set at 10 A with shorted electrodes).
Arc gap:	4 mm, maintained during burn.
Exposure:	120 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.

Analytical line	Internal standard line	Range, μ
Pt 2912.26	Rh 3051.68	100–2000
Pt 3204.04	Rh 3051.68	20–200
Pt 3064.71	Rh 3051.68	1–20
Pt 3064.71[a,b]	Rh 3051.68	0.2[c]–5
Pd 2922.49	Rh 3051.68	20–2000
Pd 3114.04	Rh 3051.68	2–50
Pd 3404.58[b]	Rh 3051.68	0.05–5
Rh 3123.70[b]	Pt 3055.32	10–1000
Rh 3323.09[b]	Pt 3055.32	0.05–10
Au 2748.26	Ag 2721.77	50–2000
Au 2748.26[a]	Ag 2721.77	5–200
Au 3122.78	Ag 2721.77	5–1000
Au 3122.78[a,b]	Ag 2721.77	1–100

[a] Measured in dark step. All other lines measured in light step.
[b] Background correction made.
[c] Residual impurity in buffer prohibits analysis below this level.

Successful exposures, fairly brief and precise, were obtained when Rh metal powder was added to the electrode. Similar control was demonstrated when Pt powder was added in place of Rh. Moving-plate studies showed Ag to be completely vaporized in 40–60 sec. The vaporization behaviors of Rh and Pt were almost identical, both appearing in the arc as the Ag was depleted.

The final method was calibrated for the determination of Pt, Pd, and Au with Rh powder added as buffer, and for the determination of Rh with Pt powder added. This technique is possible because the amounts of Pt and/or Rh usually encountered are small enough that they have no effect upon the total amount of the element in the electrode, since the amount added is relatively large (10 mg).

If a comparatively large amount of any of the three matrix elements (Ag, Rh, or Pt) should be encountered in the sample, a determination must be made and the amount added must be adjusted so that the total amount is 10 mg. This adjustment is required because these elements serve as internal standards and, therefore, must be present at essentially constant amount. For example, if the initial analysis of a sample showed 2 oz/ton (2 mg) of Pt, the amount of Pt powder added in the subsequent analysis for Rh would be reduced to 8 mg. If the sample contains high Ag, the adjustment merely involves weighing the Ag doré bead and filing or trimming to obtain the desired 10-mg size button for the spectrographic analysis. The analytical results are then calculated, taking into account the weight of the doré bead.

Precision was checked by analyzing synthetic samples that were prepared by the procedure described for standards. The results are given in Table IV. These data show the absolute capability of the method in analyzing the Ag bead. It has been found in prac-

Table IV. Analysis of synthetic samples.

Element pair	Known, μg	Found, μg[a]	Coefficient of variation, %
Pt/Rh	500	497	±2.8
	20	22.0	±5.8
Pd/Rh	500	497	±15.7
	20	20.1	±14.5
Au/Ag	500	497	±19.9
	10	9.4	±17.9
Rh/Pt	100	100	±1.8
	20	22.4	±6.6

[a] Average of 6 determinations.

tice, as expected, that the precision on actual samples may not be equal to the precision shown in the table. For example, repeated analysis of a Pt-bearing ore for Pt, Pd, Rh, and Au gave respective values of ±8%, ±19%, ±4%, and ±33% coefficient of variation. This decrease in precision is attributed principally to the well-known problem of obtaining representative splits of materials containing low-level amounts of precious metals.

Further measure of the accuracy of the method for Pt was obtained by adding tiny, accurately weighed pieces of Pt foil to fire assay blank fusion mixtures and analyzing the resulting Ag beads. The results of this test are in Table V. These data not only show that the method is quite accurate but also further demonstrate the efficiency of the fire assay for recovering Pt.

The analytical range of this method can be varied by simply changing the size of the sample put through the fire assay. For example, assuming that fire assay is limited to 2-assay-ton samples, 5 samples could be run with 2 mg of Ag added to each. Combining these 5 beads which may be accomplished by simply placing the beads in the electrode and adding the buffer would result in the regular 10 mg of Ag containing the precious metals collected from 10 assay tons. If Pd were found to be present in this bead at the spectrographic limit of 0.05 μg, the original material would contain 0.000005 oz/ton or 0.17 ppb! The analysis range is not limited at its upper end. The sample size may be reduced to the point where pure metal may be analyzed. One criterion which controls the sample size for both upward and downward extension of the analytical range is that the final 10 mg of Ag must not contain more than about 2 mg of the other precious metals, either singly or in total.

Table V. Analysis of samples of known Pt metal content.

Sample	Pt added, μg[a]	Pt found, μg[b]	Difference, μg
1	234	245	11
2	200	200	0
3	197	188	−9
4	133	134	1
5	135	127	−8
6	128	125	−3

[a] Pt weighed on assay balance, having an accuracy of ±3 μg.
[b] Single determination.

The use of high-purity Rh and Pt as buffer may appear extravagant. The cost for Rh (5–9s at $240/5 g) and Pt (5–9s at $80/5 g) figures out to 48 and 16¢ per electrode, respectively. In view of the time saved over techniques reported to date, and particularly in view of the really excellent internal standard relationship between Rh and Pt, the added expense is not considered extreme.

In summary, a method has been developed for the rapid, sensitive analysis of precious metal-bearing materials for Pt, Rh, Pd, and Au. This method combines fire-assay and spectrographic techniques to give extremely low analysis limits. Very good precision is obtained for Pt and Rh (±2%–5% coefficient of variation). For Pd, precision is adequate (±15%), but for Au somewhat poor precision (±20%) warrants use of the method only as a backup to fire assay. The analytical range of the method is extremely wide, ranging from pure metal down to <1 ppb.

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