

THE DETERMINATION OF PLATINUM METALS IN SIDERITE METEORITES

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ABSTRACT

A new technique is recorded for the quantitative determinations of the six platinum metals in siderite meteorites. The meteorite was attacked directly by perchloric acid where-by osmium and ruthenium were separated as volatile tetroxides which were collected in 3% cold hydrogen peroxide. The remaining four platinum metals were recovered by evaporation of the perchloric acid pot liquid in the presence of nitric acid, converting to chlorides and separating the base metals by cation exchange resin at $\text{pH } 1.3 \pm 0.1$. The four platinum metals were separated from each other by first carrying out a solvent extraction of diethyldithiocarbamate complexes of platinum and palladium with chloroform and then separating rhodium from iridium by reduction with copper powder. Each of the six platinum metals was finally determined spectrophotometrically.

INTRODUCTION

The siderite type of iron meteorites may contain each of the six platinum metals. Sandell (1944) found 3 ppm of osmium in a Canyon Diablo meteorite. Herr *et al.* (1960) reported the osmium content of a number of iron meteorites such as Henbury, Odessa, Canyon Diablo, etc. to be in the range of 1-3 ppm. These authors used 10% CrO_3 as the oxidant for the distillation of osmium tetroxide. Goldberg *et al.* (1951) examined siderite meteorites and found the palladium content to be in the range 1.44-7.73 ppm. In a second publication Brown and Goldberg (1949) reported the palladium concentrations of two Canyon Diablo meteorites as 3.98 ppm and 5.30 ppm and that of two Henbury meteorites as 3.30 and 2.02, respectively, each determined by neutron activation analysis. The results by Brown and Goldberg (1949) for palladium in Canyon Diablo and Henbury correspond to those found by the present author in Canyon Diablo No. I and Henbury No. I.

Hawley (1939) recorded an interesting discussion concerning the compositions and the relationships of constituents of siderite meteorites. A combination method of assay is described which, applied to siderite meteorites could provide only very approximate values for total platinum metals. The author emphasized the difficulties incident to the determination of constituent platinum metals. Many of these difficulties have only recently been overcome and at the present time the most accurate methods of separation and determination involve only wet procedures. The inclusion of a classical fire assay can only encourage losses of such metals as iridium, ruthenium and particularly osmium for which latter separation the method is completely unacceptable.

Recently a variety of techniques have been reported for the determina-

tion of trace amounts of the six platinum metals in the presence of large proportions of such base metals as iron, copper and nickel. Westland and Beamish (1957) recorded a procedure which could be applied for the determination of microgram amounts of the six platinum metals subsequent to their separation from base metals. The development of ion-exchange techniques, as described by Coburn, Beamish and Lewis (1956), Marks and Beamish (1958) etc. has resulted in analytical methods which can be used for the en masse isolation of the platinum metals.

The dissolution of such alloys as iron meteorites presented a problem. Since nitric acid is an effective reagent and since the volatile osmium octavalent oxide is simultaneously produced one would expect that this acid is particularly useful for the dissolution of meteorites. However, Sandell (1944) found that alloys so treated yield low osmium values, presumably through the decomposition products of nitric acid with iron.

While meteorites are attacked by hydrochloric and sulfuric acids the large amount of chloride ion retards the evolution of both octavalent oxides of osmium and ruthenium. In certain cases sulfuric acid has failed to effect complete dissolution of the meteorites.

Kavanagh and Beamish (1960) found perchloric acid an effective reagent for the dissolution of, and complete distillation of osmium and ruthenium from a synthetic iron-copper-nickel button. The present authors have used perchloric acid for the separation of osmium and ruthenium from synthetic iron-copper-nickel alloys containing all six of the platinum metals. The perchlorate pot liquid was evaporated in the presence of nitric acid and converted to chlorides by evaporation with hydrochloric acid. The base metals were separated at $\text{pH } 1.3 \pm 0.2$ by Dowex-50 \times 8 cation exchange resin and the platinum metals were recovered from the effluents by a combination of solvent extraction as described by Yoe and Kirkland (1954) and copper powder reduction as described by Tertipis and Beamish (1960). This method was used for the determination of the platinum metals in various types of siderite meteorites. Prior to its use for this purpose the procedure was proved by applying it to synthetic iron-copper-nickel alloys containing known amounts of each of the six platinum metals. The alloys were prepared by fusion of a mixture of the oxides of the base metals, sodium carbonate, carbon and borax, salted with each of the platinum metals and fused in a gas fired furnace at about 1450°C . The percentages of iron, copper and nickel could vary widely but in general these were respectively 56, 20 and 24. These percentages were used to allow an examination of the collecting capacity of the base metal content generally associated with the platinum metals in natural occurrences. While cobalt was not included, its presence, like that of nickel, would encourage the collecting capacity. The details of the prep-

aration have been described in various publications, Kavanagh and Beamish (1960) etc. Table No. I illustrates the accuracy of recovery for each of the six metals.

EXPERIMENTAL

Apparatus. A Beckman model B Spectrophotometer was used for absorbance measurements. All pH measurements were carried out with a Beckman model H, pH meter. Distillation apparatus used was that reported by Westland and Beamish (1957)

Reagents and materials. Reagent grade perchloric acid (70%); distilled hydrobromic acid; hydrogen peroxide (30%) and stannous chloride were used. All organic reagents used for colorimetric determination of the platinum metals were of highest purity available.

Anthranilic acid (sodium salt solution). A 2% aqueous solution of the reagent was prepared by dissolving 2 g of the recrystallized reagent of m.p. 145° C. in 100 ml of water by the addition of the required amount of sodium carbonate and then filtering.

Buffer solution. Buffer solutions of pH 2.2 ± 0.2 were prepared by the method of Yoe and Kirkland (1954) and that of pH 3.42 was obtained by mixing 95 ml of 0.2 N acetic acid with 5 ml of 0.2 N sodium acetate.

Standard Solutions

(1) *Osmium.* A stock solution of osmium was obtained by dissolving ammonium chloroosmate in 1 N hydrochloric acid. This solution was filtered and its osmium content determined by thionalide, as described by Hoffman, *et al.* (1953).

(2) *Ruthenium.* The ruthenium content of a stock solution of ruthenium bromide was obtained by thionalide as described by Rogers *et al.* (1940).

(3) *Platinum.* A weighed quantity of platinum sponge was dissolved in aqua regia and nitric acid was expelled by three evaporations with hydrochloric acid. A few drops of hydrochloric acid were added to the residue and the solution was then diluted to a measured volume with acidulated water containing 1 ml of concentrated hydrochloric acid per liter. The platinum content was determined by the thiophenol method, as described by Currah *et al.* (1946).

(4) *Palladium.* The palladium content of palladous chloride solutions in 0.15 N hydrochloric acid was determined by dimethylglyoxime as described by Wunder and Thüringer (1913).

(5) *Rhodium.* Rhodium chloride was dissolved in water containing 10

TABLE I. RECOVERY OF MICROGRAM AMOUNTS OF THE SIX PLATINUM METALS CONTAINED IN ALLOYS WITH IRON, COPPER AND NICKEL

Alloy grams	Osmium, μg		Ruthenium, μg		Platinum, μg		Palladium, μg		Rhodium, μg		Iridium, μg	
	Taken	Re- covered	Taken	Re- covered	Taken	Present in ali- quot	Found in ali- quot	Taken	Present in ali- quot	Taken	Present in ali- quot	Found in ali- quot
25	100	98	100	98	100	50	50	100	50	100	50	49
27	100	99	100	100	100	50	49	100	50	100	41	48
27.5	100	98	100	98	100	50	48	100	50	100	50	48
26	500	505 ¹	500	490 ¹	500	50	49	500	50	500	50	49
25	500	495 ¹	500	500 ¹	500	50	48	500	50	500	49	48
24.5	500	500 ¹	500	495 ¹	500	50	50	500	50	500	50	49

¹ Analyzed from aliquots.

ml of concentrated hydrochloric acid per liter and the rhodium content was determined by 2-thiobarbituric acid as described by Currach, McBryde, Cruikshank and Beamish (1946).

(6) *Iridium*. Ammonium iridium chloride was dissolved by warming in water containing 10 ml of concentrated hydrochloric acid and its iridium value was found by precipitation with 2-mercaptobenzothiazole, as described by Barefoot *et al.* (1951).

Microgram amounts of platinum metals in solution were obtained by freshly diluting the stock solution with water containing 10 ml of hydrochloric acid per liter. Aged stock solutions of microgram amounts of iridium were found to give low results by the stannous chloride-hydrobromic acid method, described by Marks and Beamish (1958) and by Berman and McBryde (1956).

Procedure. The extremely hard siderite meteorites were either cut into small pieces by an electric saw or drilled by machine taking care not to contaminate with any foreign material. An accurately weighed quantity of the sample was placed in a 1 liter distillation flask and 100 ml of water were added to the trap. The three receivers contained, respectively, 30, 10, 10 ml of 3% hydrogen peroxide cooled by ice. Water was allowed to run through the condenser and a stream of air was slowly sucked through the whole system. Forty ml of 70% perchloric acid were added to the distillation flask and it was gently heated with a very low flame. When reaction became a little vigorous, heating was discontinued and the stopcock for the incoming air into the distillation flask was closed, while a gentle suction was applied through the system. At this stage extreme care should be taken with the heating technique since slight overheating may cause explosion. The meteorites Casas Grandes (Mexico) and Grant Iron (New Mexico) reacted very violently at this stage, but with careful control of the flame and constant attention explosions were avoided. When the vigorous reaction subsided, an additional 100 ml of perchloric acid were added and the solution was boiled for 2 hours. Fifteen ml of perchloric acid were added to the trap and it was boiled for 25 minutes using low suction.

(1) *Separation of osmium from ruthenium*

The receiving solutions were quickly transferred to another previously chilled distillation flask by washing with cold 5% sulfuric acid. Sulfuric acid was removed from the receivers and connecting tubes by washing with water. One hundred ml. of water containing 20 ml of 1% potassium permanganate were placed in the trap and 30, 10 and 10 ml of hydrobromic acid, cooled in ice, were added to the three receivers. Five ml of

concentrated sulfuric acid and 40 ml of 30% hydrogen peroxide were added to the distillation flask and octavalent osmium oxide was distilled by gentle boiling for 30 minutes. The trap was then boiled for 25 minutes.

(2) *Determination of osmium*

The receiving solutions were transferred to a 250 ml beaker by washing with 10% hydrobromic acid. Two ml of 2% sodium chloride were added and, after evaporating to 5 ml on the steam bath, the solution was transferred to a 30 ml beaker and evaporated again to a moist residue. Five ml water, were added followed by 5 ml of 2% anthranilic acid (sodium salt) and the pH adjusted to 2.2 with a pH meter. Any precipitate was dissolved by adding a little dilute sodium hydroxide and the pH was again adjusted to 2.2 by dilute hydrochloric acid. The solution was then heated on the steam bath for 20 minutes, cooled in water, transferred to a 25 ml flask and the volume made up to the mark with the buffer of pH 2.2 ± 0.2 . The optical density was measured at 460 $m\mu$ against a blank distillation product treated by the same procedures as described above. The osmium content was determined with reference to a calibration curve prepared by distillation of 0, 25, 50, 75, 100 micrograms of osmium from ammonium chlorosmate with 10 ml of concentrated sulfuric acid and 40 ml of 30% hydrogen peroxide.

The method was checked with the thiourea procedure by distilling osmium from Canyon Diablo No. 1 and 2 and collecting the osmium tetroxide in 2% thiourea solution in 1 to 1 ethyl alcohol-hydrochloric acid as recommended by Westland and Beamish (1954). The results were found to be in good agreement.

(3) *Recovery and determination of ruthenium*

Ten ml of concentrated sulfuric acid and 20 ml of sodium bromate were added to the distillation flask and ruthenium was distilled by gently heating for 1 hour and collecting the ruthenium tetroxide in four receivers containing 50, 30, 10, 10 ml of 1:2 hydrochloric acid and about 3% hydrogen peroxide. The contents of the receivers were transferred to a 600 ml beaker, tightly covered with a watch glass and heated on the steam bath until the effervescence ceased. The solution was then evaporated to 5 ml in the presence of 2 ml of 2% sodium chloride. The solution was transferred to a 30 ml beaker and again evaporated on the steam bath to a moist residue, diluted to 5 ml and after treating with 5 ml of 2% anthranilic acid the pH was adjusted to 3.42. Any precipitate was dissolved by adding a little dilute sodium hydroxide and again adjusting to pH 3.42. The solution was then heated for 20 minutes on the steam bath, cooled to room temperature, transferred to a 25 ml flask and

the volume made up with buffer of pH 3.42. The optical density was measured at 620 $m\mu$ against a blank distillation product treated similarly. The ruthenium content was found from a standard curve prepared by distillation of ruthenium tetroxide from a known amount of ruthenium bromide by concentrated sulfuric acid and sodium bromate and collected as stated above.

(4) *Recovery and determination of platinum, palladium, rhodium and iridium from the perchloric acid pot liquid*

The perchloric acid pot liquid was transferred to a 600 ml beaker, covered with a rapid evaporating clock glass and, after adding 10 ml of concentrated nitric acid, the solution was evaporated to dryness over a low flame in a specially constructed all steel fumehood provided with a good suction and a safety glass window. When perchloric acid fumes were expelled, the mass was cooled and treated with 30 ml of concentrated hydrochloric acid and evaporated on the steam bath. The residue was then heated on a hot plate to remove perchloric acid fumes. The treatments with concentrated hydrochloric acid and evaporation on a steam bath and hot plate were continued until all perchloric acid was removed. The residue was then dissolved in a small amount of concentrated hydrochloric acid, diluted a little and filtered. The residue was ignited, reduced in hydrogen, chlorinated in the presence of sodium chloride, dissolved in 0.1 N hydrochloric acid, filtered through a small glass fiber filter paper and the filtrate combined with the main filtrate. The solution was diluted with water to adjust the pH to 1.3 ± 0.1 and then passed through a Dowex-50 \times 8 cation exchange resin 70 cm deep and 4 cm in diameter and washed with $1\frac{1}{2}$ liters of hydrochloric acidulated water of pH 1.5. The effluent was evaporated to 5 ml and set aside. It was found necessary to pass the base metal solution twice through the ion exchanger to separate the platinum metals quantitatively. The base metals were collected into a second receiver by washing the column with $3\frac{1}{2}$ liters of 3 N hydrochloric acid. The solution was then evaporated to 10–20 ml on a hot plate, transferred to a 600 ml beaker and after adjusting the pH to 1.3 ± 0.1 again passed through the cation exchange column and washed with $1\frac{1}{2}$ liters acidulated water of pH 1.5. The effluent was evaporated to 5 ml, mixed with the first effluent, and the combined solution was evaporated to dryness on steam bath in the presence of 5 ml of 2% sodium chloride. The organic matter was destroyed by heating with nitric acid and 30% hydrogen peroxide on a steam bath. The residue was heated on a hot plate to expel any remaining perchloric acid, and then treated with concentrated hydrochloric acid and evaporated to dryness on the steam bath. This process was repeated three times. The residue was treated with

2-3 drops of concentrated hydrochloric acid and after diluting to pH 1.3 the solution was passed through a small cation exchange column, 20 cm deep and 2 cm in diameter to separate any trace of base metals and the column was washed with 200 ml of hydrochloric acid water of pH 1.5. The effluent was evaporated to dryness on the steam bath in the presence of 5 ml of 2% sodium chloride and the organic matter was destroyed by heating cautiously with nitric acid and hydrogen peroxide and the residue was then converted to chlorides by evaporating three times with hydrochloric acid.

The residue was transferred into a 50 ml separatory funnel by treating first with 5 ml of concentrated hydrochloric acid and then with 10 ml of water. Platinum and palladium were separated from rhodium and iridium by chloroform extraction of their diethyldithiocarbamate complexes by the method of Yoe and Kirkland (1954). Platinum and palladium were then separated from each other by the solvent extraction of palladium *p*-nitrosodimethylaniline complex in the cold and finally both were determined spectrophotometrically by the *p*-nitrosodimethylaniline method of Yoe and Kirkland (1954).

The solution in the separatory funnel containing rhodium and iridium was washed into a 250 ml beaker and evaporated to dryness in the presence of 2 ml of 2% sodium chloride. The organic matter was destroyed by fuming nitric acid and hydrogen peroxide and finally the metals were converted to chlorides by evaporation with concentrated hydrochloric acid three times; all these operations being carried out on the steam bath.

The chlorides of rhodium and iridium were dissolved in 20 ml of 1 N hydrochloric acid and rhodium was separated from iridium by copper powder and then finally determined by the method of Tertipis and Beamish (1960). For maximum accuracy it was found that iridium should be oxidized both before and after passing through the ion exchange column. After the separation of rhodium from iridium by copper powder, iridium remains in the filtrate in the reduced state and if this iridium containing copper ion is passed through the ion exchange column without prior oxidation to iridium (IV) it was found that some iridium was absorbed on the resin bed. Failure to oxidize iridium after passing through the column, which also reduces it, leads to incomplete development of color with stannous chloride-hydrobromic acid.

The above solvent extraction method was tested with known micro amounts of platinum, palladium, rhodium and iridium and some of the data are recorded in Table I.

The results of the analysis of the meteorites are given in Table II.

TABLE II. PLATINUM METALS CONTENT OF SOME SIDERITE METEORITES

Name and origin of the meteorite	Weight taken, g	Found, microgram						Present in ppm					
		Os	Ru	Pt	Pd	Rh	Ir	Os	Ru	Pt	Pd	Rh	Ir
Canyon Diablo No. 1 (Arizona)	9.6656	48	—	50	49.6	37.5	20	4.98	—	5.17	5.1	3.88	2.60
Canyon Diablo No. 2 (Arizona)	11.8024	46	—	22	32	25	18	3.90	—	1.86	2.71	2.12	1.53
Henbury, No. 1 (McDonnell Ranges, Central Australia)	7.8773	133.5	40	30	17	18.5	54	17	5	11.4	2.2	2.3	6.85
Henbury, No. 2 (Australia)	9.9676	100.0	—	74	10	31.2	26	10	—	7.42	1.20	3.13	2.60
Trenton (Washington, Wis.)	10.0024	35.2	94	84	66	41	34	3.52	9.4	8.4	6.6	4.1	3.4
Casas Grandes (Mexico)	10.8030	51.2	—	116	28	31.2	14	4.74	—	10.7	2.6	2.9	1.3
Grant Iron (New Mexico)	10.8184	26	21.6	—	18	27.6	—	2.4	2.0	—	1.66	2.55	—

CONCLUSION

The applicability of a wet analytical method for the determination of the six platinum metals in iron-nickel-copper alloys has been demonstrated. The method is found particularly suitable for the dissolution of siderite meteorites as well as for the separation and determination of the platinum metals in these alloys.

The data in Table II show that all of the siderite meteorites examined contain platinum metals.

Concentration ranges of the platinum metals in the seven siderite meteorites examined were found to be as follows: osmium—2.4 to 17 ppm; ruthenium—0 to 9.4 ppm; platinum—1.86 to 11.4 ppm; palladium—1.20 to 6.6 ppm; rhodium—2.12 to 4.1 ppm; iridium—1.3 to 6.85 ppm.

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