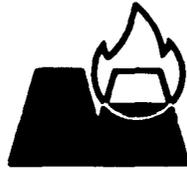


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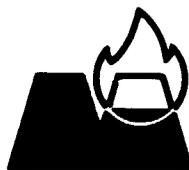
**THE DETERMINATION, BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY
USING ELECTROTHERMAL ATOMIZATION, OF PLATINUM,
PALLADIUM, RHODIUM, RUTHENIUM, AND IRIDIUM**

by

J. Haines and R.V.D. Robért

28th May, 1982

**COUNCIL FOR MINERAL TECHNOLOGY
200 Hans Strijdom Road
RANDBURG
South Africa**



MINTEK

(ANALYTICAL CHEMISTRY DIVISION)

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RUTHENIUM, AND IRIIDIUM**

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SYNOPSIS

A method that involves measurement by atomic-absorption spectrophotometry using electrothermal atomization has been developed for the determination of trace quantities of platinum, palladium, rhodium, ruthenium, and iridium in mineralogical samples. The elements are separated and concentrated by fusion, nickel sulphide being used as the collector, and the analyte elements are measured in the resulting acid solution. An organic extraction procedure was found to offer no advantages over the proposed method. Mutual interferences between the five platinum-group metals examined, as well as interferences from gold, silver, and nickel were determined. The accuracy of the measurement was established by the analysis of a platinum-ore reference material.

The lower limits of determination of each of the analyte elements in a sample material are as follows: platinum $1,6 \mu\text{g/l}$, palladium $0,2 \mu\text{g/l}$, rhodium $0,5 \mu\text{g/l}$, ruthenium $3 \mu\text{g/l}$, and iridium $2,5 \mu\text{g/l}$. The relative standard deviations range from 0,05 for rhodium to 0,08 for iridium.

The method, which is described in detail in the Appendix, is applicable to the determination of these elements in ores, tailings, and geological materials in which the total concentration of the noble metals is less than 1 g/t.

SAMEVATTING

Daar is 'n metode vir die bepaling van spoorhoeveelhedes platinum, palladium, rodium, rutenium en iridium in mineralogiese monsters ontwikkel wat meting deur atoomabsorpsiespektrofotometrie met gebruik van elektrotermiese verstuiwing behels. Die elemente word geskei en deur smelting gekonsentreer met nikkelsulfied as die versamelaar en die analietelemente word in die resulterende suuroplossing gemeet. Daar is gevind dat 'n organiese ekstraksieprosedure geen voordele bo die voorgestelde metode bied nie. Daar is wedersydse steurings tussen die vyf platinumgroepmetale wat ondersoek is, asook steurings deur goud, silwer en nikkels bepaal. Die akkuraatheid van die meting is deur die ontleding van 'n platinumertsverwysingsmateriaal bepaal.

Die onderste opspoorgrens van elkeen van die analietelemente in 'n monstermateriaal is soos volg: platinum $1,6 \mu\text{g/l}$, palladium $0,2 \mu\text{g/l}$, rodium $0,5 \mu\text{g/l}$, rutenium $3 \mu\text{g/l}$, en iridium $2,5 \mu\text{g/l}$. Die relatiewe standaardafwykings wissel van 0,05 vir rodium tot 0,08 vir iridium.

Die metode wat in besonderhede in die Aanhangsel beskryf word, kan toegepas word op die bepaling van hierdie elemente in ertse, uitskotte en geologiese materiale waarin die totale konsentrasie van die edelmetale minder as 1 g/t is.

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1. INTRODUCTION

The noble metals, i.e., gold and the platinum-group metals (PGM) — platinum, palladium, rhodium, ruthenium, iridium, and osmium — have been analysed in a wide variety of materials (e.g., tailings, flotation concentrates, and mattes) at the Council for Mineral Technology (Mintek), formerly the National Institute for Metallurgy (NIM). Several methods have been developed and are used routinely. However, problems are still encountered in the determination of trace amounts of the elements (i.e., when the total noble-metal concentrations are lower than 1 g/t) in tailing or borehole-core samples.

The common method used in the preparation and concentration of samples is a fire-assay technique, with lead as the collector¹ when only platinum, palladium, rhodium, and gold are to be determined, and with nickel sulphide as the collector² when all seven PGM are to be determined.

Most existing methods for the measurement of the noble metals, e.g., flame atomic-absorption spectroscopy (AAS) or optical emission spectroscopy (OES) with an inductively coupled plasma (ICP) source, are not sufficiently sensitive when the noble-metal content is lower than 1 g/t, and require large masses of sample material (up to 1 kg). Consequently, several fire-assay fusions are necessary (a maximum of 50 g of sample material can be fused at a time), after which the separated noble metals are combined for measurement.

A method involving neutron activation was developed that has extremely good sensitivity (with limits of determination ranging from 10 μ g of platinum per litre to 0,10 μ g of iridium per litre) for most of the noble metals, but it also requires preconcentration by fire assay, and is not ideally suited to routine operations.

Electrothermal atomization (ETA) used with atomic-absorption spectrophotometry (AAS) is up to 100 times more sensitive than is flame AAS, and would enable traces of the noble metals to be measured in solution. However, a thorough survey of the available literature showed that there were extreme differences of opinion with regard to interferences³⁻⁵; that, in general, each method was suitable for the determination of only one of the noble metals⁶⁻⁸; and that each method was specific to a particular instrument.

It became obvious that an investigation was necessary so that the following could be established:

- (1) the conditions of measurement under which the available instruments should be used,
- (2) the possible interference patterns relative to the matrix of the solutions being measured, and
- (3) the preconcentration method to be used.

In addition to preconcentration by fusion of the sample with nickel sulphide as the collector², an evaluation was carried out of an extraction technique in which *n*-octylaniline is used as the extractant. This extractant has been extensively and successfully used at Mintek as a group extractant for the noble metals⁹.

In this investigation, work on osmium was abandoned, since its analysis is seldom required; it is the least sensitive of the noble metals when measured by the use of techniques involving atomic absorption, and preliminary measurements by ETA-AAS were disappointing.

Gold was also excluded, since it had been investigated previously¹⁰.

2. EXPERIMENTAL METHOD

2.1. Apparatus and Reagents

A Pye Unicam SP9 spectrophotometer was used throughout in conjunction with an SP9 Video Furnace Programmer and an SP9 computer. Peak heights were recorded on a JJ Instruments CR652S two-pen chart recorder.

A Varian AA475 spectrophotometer was later used in conjunction with a Varian CRA90 carbon-rod atomizer (CRA) for comparison of the sensitivity and precision of the proposed method. Peak heights were recorded with a Varian Model 9176 chart recorder.

Unless otherwise stated, pyrolytically coated graphite tubes were used for all measurements. Socorex adjustable micropipettes of 5 to 25 μ l were used to transfer sample solutions to both graphite furnaces.

Separate standard stock solutions of platinum, palladium, rhodium, ruthenium, and iridium (the analytes) were prepared from pure metals or sponges (Appendix), and were diluted for use with 10 per cent (v/v) A.R.-grade hydrochloric acid. All other acids and solutions were of A.R. grade.

A BNC Portanim Model AP-2 gamma-ray scintillation counter with a thallium-drifted sodium iodide (NaITh) detector was used for all measurements of the iridium isotope.

2.2. Comparison of Organic and Aqueous Media for Determination of the Analytes by ETA-AAS

In the development of a method for the determination of the analytes by ETA-AAS, two approaches were suitable for the concentration of the analytes, as follows:

- (1) collection by fire assay and measurement by ETA-AAS in an acid medium, and

(2) collection by fire assay and further concentration by solvent extraction, followed by ETA-AAS measurement in an organic medium (which might have the added advantage of increased sensitivity).

Synthetic standard solutions were used for preliminary measurement in aqueous and organic media to establish which medium would be more suitable.

2.2.1. Measurement of the Analytes in Aqueous Solution

The dissolution of the nickel sulphide residue is effected with a mixture of hydrochloric acid and hydrogen peroxide, but for optimum atomization it might be necessary for the analytes to be measured in other acid media.

Other investigators measured the noble metals by ETA-AAS in various acid solutions^{3,4,5}, the most widely used of which seems to have been hydrochloric acid⁴⁻⁶. The concentration of the acid does not appear to be critical¹¹, so initial experiments in this investigation were carried out in 10 per cent (v/v) hydrochloric acid. Good reproducibility and sensitivity were obtained in this medium.

The analytes were also measured in 10 per cent (v/v) aqua regia (hydrochloric acid and nitric acid in a ratio of 2:1). Table 1 compares the peak heights obtained for ruthenium and iridium in these two media. It was found that the addition of nitric acid caused the reproducibility to deteriorate and, for some elements (e.g., ruthenium and iridium), it caused a decrease in sensitivity.

TABLE 1

Measurement of iridium and ruthenium in 10 per cent (v/v) hydrochloric acid and 10 per cent (v/v) aqua regia

Element	Peak heights in two media, mm	
	Hydrochloric acid 10% (v/v)	Aqua regia 10% (v/v)
Ruthenium	45	30
Iridium	65	26

Thus, the results confirmed the findings reported in the literature, namely that hydrochloric acid was the most suitable acid medium for measurement of the noble metals by ETA-AAS. All subsequent tests for the optimization of the conditions of measurement and for the study of interferences were therefore carried out in 10 per cent (v/v) hydrochloric acid.

2.2.2. Measurement of the Analytes after Their Extraction with *n*-octylaniline

It is reported that *n*-octylaniline extracts all the noble metals, as well as some of the base metals, to a greater or lesser extent, depending upon the organic solvent used¹². The solvent chosen was 1 M *n*-octylaniline in chloroform, since this appeared to be the most selective for the noble metals. However, chloroform is not ideal for use with a graphite furnace because, owing to its high volatility, one finds it difficult to inject, especially if the furnace is not quite cold. After extraction, the chloroform was therefore evaporated and the residue was dissolved in methyl isobutyl ketone (MIBK), which is more suitable for use in graphite furnaces.

For complete extraction of the analytes, especially rhodium, it is important that they should be in the correct oxidation state^{9,12}. Prior to extraction, all the analytes (in appropriate concentrations) were therefore dissolved in concentrated hydrochloric acid to which a few milligrams of sodium chlorate had been added to ensure an excessive amount of chlorine. This solution was taken twice almost to dryness on a hot-plate, and finally diluted to volume in 3N hydrochloric acid, which is the concentration required for extraction. The extraction was carried out as described elsewhere⁹.

Analysis of the residual layer of hydrochloric acid after extraction showed that rhodium was the only analyte that was not completely extracted, a recovery* of only 90 per cent being obtained for that element.

* In this report, *recovery* means amount determined as a percentage of the amount present.

The organic phase was then tested on the graphite furnace, aliquot portions of the sample being transferred to the graphite furnace with micropipettes. However, unlike an aqueous sample, which is affected by surface tension and remains as a discrete droplet in the centre of the graphite furnace, the organic solution tended to spread. This tendency limited the amount of solution that could be placed in the furnace, since volumes greater than 10 μ l tended to spill out of the furnace. The solution was also found to be much less sensitive than was an equal volume of aqueous solution. This was probably because the organic solution flowed to the extremities of the furnace, where the temperature necessary to completely volatilize the analytes could not be attained. During ashing, the *n*-octylaniline was volatilized (boiling-point 302°C) and given off as a copious, black, almost sticky smoke. This caused background problems and, since the SP9 furnace is enclosed, the furnace holders and the lenses tended to become coated after only a few analyses.

With the aerosol technique (Section 2.6), the sensitivities for organic and aqueous solutions of the same concentration were found to be similar. (This is probably because the sample is sprayed onto a hot graphite furnace, dries on contact, does not spread, and is retained in the contact zone for complete atomization.) However, the background problem was still present, and it was therefore concluded that, with regard to precision and sensitivity, measurement in an organic medium offers no real advantage over determination in an aqueous medium.

2.3. Optimization of the Conditions for Measurement with the SP9 Spectrophotometer

In the optimization of the conditions it was necessary for the following to be established:

- (1) the maximum drying temperature at which there is no physical loss of the analyte due to spitting,
- (2) the maximum ashing (pyrolysis) temperature that can be used without loss of the analyte element, and
- (3) the lowest temperature at which complete atomization of the analyte takes place.

For determination of the maximum drying temperature for the sample, 25 μ l of a synthetic standard solution of the analyte element under investigation was transferred to the graphite furnace with the aid of a micropipette. In the majority of cases, a temperature of 95°C was found to be the most suitable for drying the 10 per cent acid solution. Higher temperatures caused sputtering near the end of the drying stage and possible physical losses.

The volatilization temperature for each element was determined while the ashing temperature (the ashing time was set at 20 seconds) was varied at a constant atomization temperature (2600°C). The peak height for atomization was measured for each ashing temperature, and a lowering of the peak height was regarded as being an indication of volatilization of the particular analyte element at that ashing temperature. In the optimization of the atomization temperature, the ashing temperature was kept constant while the atomization temperature was varied (in 200°C steps) between 2200 and 3000°C.

Table 2 gives the volatilization temperature for each analyte element and the atomization temperatures at which the maximum absorbance measured was attained.

TABLE 2

Maximum ashing temperatures and optimum atomization temperatures for measurement of the analytes on the SP9 spectrophotometer

Element	Temperature, °C	
	Ashing (maximum)	Atomization (optimum)
Platinum	1700	2800
Palladium	1200	2400 to 3000
Rhodium	1600	2800
Ruthenium	1700	2800
Iridium	> 2000	2800

In practice, the ashing temperature is chosen as being the temperature at which the whole matrix or background is volatilized. For the samples analysed, this temperature was found to be 1000°C and was therefore adopted as the standard for all further work. The use of this lower ashing temperature also helped in lengthening of the life of the tube.

It was found that the temperature of atomization was not critical for palladium, so the atomization temperature could be standardized at 2800°C for all the analytes. The atomization time was set at 5 seconds, since longer times served only to reduce the useful life of the graphite furnace.

In the course of this study, a memory effect was observed (i.e., a high blank measurement after the atomization of an analyte). This effect was apparent only occasionally, but was investigated in tests with an iridium isotope.

2.3.1. Volatilization of the Iridium Isotope

Since the noble metals are known to be very refractory, the atomization of iridium was checked with the aid of the iridium isotope ^{192}Ir , which is stable and has a half-life of approximately 35 days.

Ammonium hexachloro-iridate (0.0033 g) was irradiated in a quartz vial for 92 hours and then diluted to 100 ml with 10 per cent (v/v) hydrochloric acid, giving approximately 1.4 p.p.m. of iridium in solution. (It should be noted that this is only an approximate concentration, since long irradiation times tend to alter the physical properties of some materials, and the solubility of the ammonium hexachloro-iridate was found to have decreased after irradiation.)

The gamma radiation from an unused graphite furnace was counted with a sodium iodide thallium-drifted detector to give a background count. The solution (25 μl) was transferred to the graphite furnace, dried at 95°C, and recounted. The sample was then ashed in the furnace under optimum conditions and again counted as a check for losses. Finally, the sample was atomized at 2800°C, the counts were measured, and the amount of ^{192}Ir that had been volatilized was calculated.

Initially, these experiments were carried out with the Pye Unicam SP9 system, and the counts after atomization showed a consistent loss of only 20 per cent of the iridium. Further atomization at the maximum attainable temperature of 3000°C apparently failed to volatilize more of the iridium. However, when this experiment was repeated on the Varian instrument with the CRA90, almost all the iridium was volatilized after a single atomization at 2800°C. The SP9 graphite furnace is considerably larger than the carbon rod used in the Varian CRA90 system, and therefore displays a considerably wider variation in temperature along its length. As a result it was assumed that the atomized iridium might be recondensing on the cooler ends of the tube. This was found to be so when a tube from which ^{192}Ir had been atomized was cut into three portions and each portion was counted independently: approximately 80 per cent of the original mass of iridium was found to have been transferred from the centre to the ends of the tube. However, the iridium deposited on the ends of the tube appears to play no further part in the atomization of iridium during subsequent determinations, since the ends of the graphite furnace never attain the temperature necessary to atomize the iridium, unless there is malfunctioning of the furnace (Section 4).

2.3.2. Measurement of the Analytes with Graphite Tubes Impregnated with a Refractory Metal

In the measurement of several elements, impregnated graphite tubes are reported¹³ to offer several advantages over conventional pyrolytic tubes, namely, greater sensitivity, freedom from interferences, and longer tube life. It was therefore decided that some of these coatings should be tested by the impregnation of non-pyrolytically coated tubes with various elements. The method described by Fritzche *et al.*¹³ was used in the impregnation of tubes with tungsten, molybdenum, vanadium, zirconium, titanium, and silicon.

An aliquot portion of iridium solution was dried, ashed, and atomized from each of the prepared tubes.

In the tubes impregnated with tungsten, zirconium, and molybdenum, no atomization peaks were obtained for iridium, even at a maximum atomization temperature of 3000°C. This suggests the formation of a highly refractory compound that is not volatile at the temperature of atomization.

The atomization peaks obtained for iridium in tubes impregnated with silicon and vanadium was similar to that obtained with a non-pyrolytically coated tube, whereas the atomization peak for titanium-impregnated tubes was slightly lower. However, since neither the silicon- nor vanadium-coated tubes appeared to improve the volatilization of iridium over that obtained with pyrolytically-coated tubes, this part of the investigation was not pursued.

2.4. Interference Studies

Since the fusion with nickel sulphide as the collector² effectively separates the noble metals from the base metals and other constituents in the sample material, the resulting solutions are expected to contain only the PGM, gold, silver, and a small amount (less than 10 mg) of occluded nickel. Only mutual interferences between the PGM, gold, silver, and nickel were therefore tested.

Interference was tested at ratios of interferent to analyte of 10:1 and 100:1 respectively. The latter is the maximum ratio expected to be present in typical samples of tailings from the Merensky Reef.

Measurements were made with synthetic solutions containing the analyte element alone, synthetic solutions containing the analyte element plus interferent, and synthetic solutions containing the interferent alone (to serve as a blank). Interference was considered to be present if the absorbance obtained for the solution containing the analyte plus interferent differed by more than 10 per cent from the absorbance for the solution containing the analyte alone, any measurement obtained for the blank solution being taken into consideration. Table 3 shows the interference effects for a ratio of interferent to analyte element of 100:1. There was no interference at a ratio of 10:1.

TABLE 3

Interferences at a ratio of interferent to analyte element of 100:1

Interferent	Interference on analyte element				
	Pt (0,5 p.p.m.)	Pd (0,1 p.p.m.)	Rh (0,05 p.p.m.)	Ru (0,2 p.p.m.)	Ir (0,5 p.p.m.)
Pt	-	-	M	-	-
Pd	-	-	-	-	M
Rh	-	-	-	-	M
Ru	M	-	M	-	MS
Ir	M	-	M	MS	-
Au	-	-	M	M	M
Ag	-	-	M	-	-
Ni	-	-	-	-	M

- = No significant interference; recovery 90 to 100 per cent

M = Moderate interference; recovery 50 to 90 per cent

MS = Moderate-to-severe interference; recovery 10 to 50 per cent

At a ratio of 100:1, no interference was evident for palladium; platinum, rhodium, ruthenium, and iridium all underwent moderate-to-severe interference from one or more of the other elements tested. Fortunately, in typical sample materials, the elements that undergo interferences are seldom found in the ratios given in Table 3. (For example, the ratios of these elements in ore from the Merensky Reef are platinum 60 per cent, palladium 25 per cent, gold 5 per cent, rhodium 5 per cent, ruthenium 5 per cent, and iridium 1 per cent.) The exceptions are palladium and iridium, where the ratio can be 25:1. However, the tests revealed no interference at that ratio.

Lanthanum and uranium are used as releasing agents in the determination of these analytes by flame AAS. It would be convenient for one to be able to use the solutions prepared for flame measurement on the graphite furnace, either as a cross-check on an alternative measuring technique or when the concentration of the analyte is too low for accurate measurement by flame AAS. Some experiments were therefore carried out so that the effects of both of these releasing agents on the measurement of the analytes by ETA-AAS could be determined. Uranium and lanthanum were added to the analyte solutions at the concentrations used for flame analysis (10 g/l).

For all the analytes, uranium was found to 'poison' the graphite furnace to some extent, and thus to inhibit their volatilization. It was notably worse for iridium, for which, after an addition of uranium in solution to the graphite furnace, no peaks could be obtained for any atomizations of iridium. Atomization of the graphite furnace at the maximum temperature (3000°C) for up to 20 seconds could not remove this effect. It appears that the uranium, which is very non-volatile, forms complexes and inhibits the volatilization of the analytes from the graphite furnace.

Lanthanum also suppressed the atomization peaks for all the analytes. In most cases, prolonged heating of the graphite furnace at 3000°C was found to remove the lanthanum, but this treatment severely limits the usability of the graphite furnace.

No uranium nor lanthanum must therefore be present during ETA-AAS, since even a concentration of 0,1 g of uranium or lanthanum per litre was found to interfere with the measurement of iridium.

2.5. Applicability of the Aerosol Technique

An alternative method for the introduction of the sample to ETA was developed by Matousek¹⁴, modified for use with the Varian CRA90¹⁵, and used extensively at Mintek. The sample is sprayed as an aerosol into the graphite tube, thus obviating the use of micropipettes, and offers the advantages of improved precision and sensitivity.

The system was adapted for use with the SP9 by the drilling of a hole in the front of the furnace door through which a machined tantalum nozzle can be inserted and aligned with the orifice of the graphite tube. The system was tested for iridium.

The tests were carried out at a wavelength of 264,0 nm, which, although less sensitive than the 208,9 nm line, is less prone to background interference. It was hoped that the aerosol technique would improve the sensitivity. The optimum distance between the end of the tantalum-spray tube and the graphite tube was found to be 1,5 mm, and a spraying time of 30 seconds was found to give the best sensitivity and precision. The conditions for measurement were altered to allow the sample to dry completely before atomization (Table 4).

TABLE 4

Altered furnace conditions for measurement of the sample

Treatment	Temperature, °C	Time, s	Ramp rate, °C/s
Drying	150	40	5
Ashing	1000	30	20
Atomizing	2800	5	1000

A calibration curve was obtained for iridium, and the limit of determination was calculated as being 0,05 p.p.m. This indicated that there had been some improvement in sensitivity over that of 0,08 p.p.m., obtained at the same wavelength but with micropipettes to effect transfer of the solution to the furnace. The precision was calculated and found to be comparable with that obtained when micropipettes were used. This system has the disadvantage that it is unsuitable for small volumes of sample.

In the SP9, since the furnace system is enclosed and the sprayed solution tends to spread around the inside of the assembly, it was necessary for the inside of the furnace to be cleaned after use. The lenses and windows, especially, needed 'defogging', and the area behind the metal plate at the back of the graphite furnace also required cleaning.

2.6. Comparison of the Pye Unicam SP9 System with the Varian CRA90 System for Measurement of the Analytes by ETA-AAS

Under the conditions that had been optimized on the SP9 for drying, ashing, and atomizing, the analytes were measured on the Varian CRA90 (in conjunction with a Varian AA475 spectrophotometer), and the results compared with those obtained by use of the SP9 system. The amounts of synthetic standard solution used for measurement on the CRA90 and SP9 systems were 10 and 25 μ l respectively. Table 5 compares the two systems of measurement.

Iridium was evaluated at both wavelengths on the SP9 because, at the lower wavelength, the background effects for some of the samples analysed were very severe, being in the form of double atomization peaks. In some samples, iridium therefore had to be measured at the less sensitive wavelength.

Comparison of the results in Table 5 shows that in every case the sensitivity and precision of the results are considerably better for the SP9 system than they are for the Varian CRA90 system. Admittedly, 25 μ l of solution is used with the SP9, whereas only 10 μ l is used with the CRA90, but it is obvious from the results that, even with the same amount of solution used on each of the instruments, better sensitivity would be obtained with the SP9.

3. RESULTS

So that the accuracy of the method could be determined, three samples were analysed by the method described in the Appendix, and the results for the individual analytes were compared with the recommended values. The samples included the reference material SARM 7 (which consists of ore from the Merensky Reef) and two low-grade samples (one of which was a sample of chromite ore) that had been extensively analysed at Mintek by flame AAS. Table 6 gives the results of this analysis.

DETERMINATION BY ETA-AAS

TABLE 5

Comparison of the Pye Unicam SP9 and Varian CRA90 systems for the measurement of five PGM by ETA-AAS

Element	Linear range of calibration mg/l		Detection limit in soln mg/l		Determination limit in soln mg/l		s_r (n = 10)	
	Varian CRA90	Pye Unicam SP9	Varian CRA90	Pye Unicam SP9	Varian CRA90	Pye Unicam SP9	Varian CRA90	Pye Unicam SP9
Platinum	0 to 2	0 to 0.4	0.012	0.308	0.025	0.016	0.05(0.5)	0.07(0.016) 0.05(0.3)
Palladium	0 to 0.5	0 to 0.06	0.01	0.001	0.02	0.002	0.15(0.1)	0.13(0.002) 0.08(0.02)
Rhodium	0 to 0.2	0 to 0.05	0.012	0.002	0.025	0.005	0.09(0.1)	0.05(0.005) 0.04(0.05)
Ruthenium	0 to 0.4	0 to 0.1	0.03	0.015	0.06	0.03	0.33(0.1)	0.05(0.03) 0.65(0.05)
Iridium (208.9 nm line)	0 to 1	0 to 0.3	0.10	0.012	0.20	0.025	0.25(0.5)	0.08(0.025) 0.08(0.1)
Iridium (264.0 nm line)		0 to 0.3		0.04		0.08		0.08(0.08) 0.07(0.1)

s_r = Relative standard deviation

n = Number of determinations

Notes:

The detection limit is taken as being twice the average blank value of a used graphite furnace

The determination limit is taken as being four times the average blank value of a used graphite furnace

Figures in parentheses represent the concentrations, in parts per million, at which the relative standard deviations were calculated

TABLE 6

Results of analysis of three samples

Element	Sample no.	Analytical results, p.p.m.	Recommended values, p.p.m.	Number of analyses
Pt	H666	0.60 ± 0.07	0.58(0.60)	5
	H100	0.38 ± 0.06	0.45	7
	SARM 7	3.75 ± 0.12	3.74 ± 0.045	8
Pd	H666	0.41 ± 0.06	0.41(0.47)	5
	H100	0.18 ± 0.03	0.20	6
	SARM 7	1.46 ± 0.05	1.53 ± 0.032	10
Rh	H666	0.08 ± 0.006	0.08(0.11)	4
	H100	0.02 ± 0.001	0.02	7
	SARM 7	0.22 ± 0.02	0.24 ± 0.013	10
Ru	H666	0.25 ± 0.02	0.27(0.30)	5
	H100	0.06 ± 0.004	0.06	7
	SARM 7	0.45 ± 0.05	0.43 ± 0.057	10
Ir	H666	0.022 ± 0.0008	<0.16	4
	H100	0.008 ± 0.002	0.02	7
	SARM 7	0.061 ± 0.004	0.074 ± 0.012	10

The figures in parentheses are the values determined by another laboratory

In view of the precision of measurement (Table 5) and, in some instances, the very low concentration of the particular analyte in the sample (e.g., iridium in H100 and SARM 7), the values obtained compare very favourably with the recommended values.

4. DISCUSSION

ETA-AAS has the advantage of extremely good sensitivity. Unlike most of the other available measurement techniques, e.g., flame AAS and OES-ICP, the five PGM investigated can be measured after the fire-assay fusion of a 50 g sample of tailing material. Instrumental neutron-activation analysis (INAA) also has sufficient sensitivity for this to be accomplished, but is not as sensitive for some of the PGM (e.g., platinum, palladium, and rhodium) as is ETA-AAS; in addition, by its nature, the technique is not well suited to routine analysis.

Table 7 gives a comparison of the limits of determination for the four analytical techniques in the determination of 50 g of sample.

TABLE 7

Comparison of the limits of determination for five PGM by ETA-AAS, flame AA spectroscopy, INAA, and OES-ICP in 50 g samples of powdered ore

Element	Limit of determination, $\mu\text{g/l}$			
	ETA-AAS	Flame AAS	INAA	OES-ICP
Pt	1,6	1000	10	40
Pd	0,2	100	4	30
Rh	0,5	100	1	25
Ru	3,0	500	10	125
Ir	2,5(8,0)	750	0,1	160

The figure in parentheses is the value obtained on the less sensitive wavelength

On certain occasions during the investigation, high and variable blank values were obtained for most of the analytes when they were measured by ETA-AAS. At first, these were thought to be memory effects as a result of incomplete volatilization. However, the good precision and the reproducible straight lines obtained for the calibration graphs in spite of these blank values conflicted with this view. The experimental work carried out with the radioactive tracer (Section 2.3.1) showed that the iridium was volatilized during atomization, but that it subsequently condensed on the cooler ends of the graphite tube, where it probably accumulated but did not interfere with subsequent measurements, since the ends of the tube do not usually attain a temperature high enough to cause volatilization. However, after prolonged use with acid solutions, the metal contact clamps supporting the graphite tube become pitted and their electrical contact with the tube is poor. This results in arcing, which causes the temperature to increase at the points of contact, i.e., at the ends. Under these conditions, some of the condensed analyte might volatilize and give rise to a blank measurement. This problem can be overcome only by the installation of a new set of contact clamps.

It was found that the time taken to dry a particular volume of solution on the SP9 system varied according to the temperature of the graphite tube at the time the sample was introduced. If the sample solution was introduced some time after opening of the furnace door had allowed the tube to reach room temperature, a longer drying period was found to be necessary than when the sample was introduced to a warm tube as soon as the door had been opened. The procedure should be standardized so that problems of this type do not arise.

5. CONCLUSIONS

The AAS method using ETA, which is reported here, is suitable for the determination of trace quantities of platinum, palladium, rhodium, ruthenium, and iridium in mineralogical samples. In the graphite furnace, measurement of these metals in an aqueous solution is more precise and practicable than is measurement after organic extraction.

Although mutual interferences occur when the ratios of interferent to analyte are high, analysis of the analytes is free of interference at the concentrations normally encountered in most samples. The method is applicable to a Pye Unicam SP9 system and to a Varian CRA90 system. The precision and sensitivity of the Varian system are lower, and should be amenable to any system incorporating a graphite furnace.

The method is sensitive (the limits of determination range from 2 $\mu\text{g/l}$ for palladium to 25 $\mu\text{g/l}$ for iridium) and precise (with relative standard deviations around 0,07 to 0,08), and the results obtained for the analysis of a certified reference material compare favourably with the recommended values for each of the five PGM determined.

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APPENDIX

E.1. Platinum

THE DETERMINATION, BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY USING ELECTROTHERMAL ATOMIZATION, OF PLATINUM, PALLADIUM, RHODIUM, RUTHENIUM, AND IRIDIUM
LABORATORY METHOD NO. 78/30

1. OUTLINE

The platinum-group metals (PGM) are separated by the use of a fire-assay technique with nickel sulphide as the collector¹. The nickel sulphide button is crushed and dissolved in hydrochloric acid, but the PGM sulphides remain undissolved. These sulphides are then dissolved in hydrochloric acid and hydrogen peroxide, and platinum, palladium, rhodium, ruthenium, and iridium are measured individually by atomic-absorption spectrophotometry (AAS) using electrothermal atomization (ETA).

2. APPLICATION

The method is applicable to the determination of platinum, palladium, rhodium, ruthenium, and iridium in ores, tailings, and borehole cores that are unsuitable for flame atomic-absorption spectroscopy (AAS) because the PGM concentration is too low (i.e., below 1 µg/g) or because there is insufficient sample. A Pye Unicam SP9 system was used in the development of the method, which is, however, also applicable to the Varian CRA90 system.

Total time for analysis of 1 sample 3 to 4 days, and for
10 samples 4 to 5 days.

3. AMOUNT OF SAMPLE

The amount of sample to be taken for the analysis of platinum, palladium, rhodium, ruthenium, and iridium depends upon its estimated PGM content. The method was designed for use with 1 p.p.m. or less of the total PGM plus gold (the noble metals), in which case 50 g of sample should be used. It was also used for the analysis of a reference material SARM 7, which has a total PGM content of approximately 6 p.p.m.; for this analysis 10 g of sample was used. Higher concentrations of PGM would therefore require smaller amounts of sample for analysis provided that the sample was homogeneous.

4. APPARATUS

(1) *Pye Unicam SP9 Atomic-absorption Spectrophotometer*

Fitted with simultaneous background correction, SP9 computer, SP9 Video furnace, and a two-pen chart recorder (JJ Instruments CR652S).

(2) *Socorex Adjustable Micropipette, 5 to 50 µl*

5. REAGENTS

(1) *Hydrochloric Acid, 37 per cent*

A.R. grade.

(2) *Hydrochloric Acid, 10 per cent (v/v) and 40 per cent (v/v) Solutions*

Dilute concentrated hydrochloric acid as required.

(3) *Platinum and Palladium Stock Standard Solutions, 1000 mg/l*

Dissolve 1 g of pure metal in aqua regia (a mixture of hydrochloric and nitric acids in a ratio of 3:1).

Take to incipient dryness three times on a hot-plate with concentrated hydrochloric acid. Dilute to volume in a 1-litre flask with 40 per cent (v/v) hydrochloric acid.

(4) *Rhodium, Ruthenium, and Iridium Stock Standard Solutions, 1000 mg/l*

Prepare as described in Laboratory Method No. Pt 78/2.

(5) *Diluted Stock Standard Solutions*

Dilute stock standard solutions to the following appropriate concentrations with 10 per cent (v/v) hydrochloric acid: platinum 0 to 0,4 mg/l, palladium 0 to 0,06 mg/l, rhodium 0 to 0,05 mg/l, ruthenium 0 to 0,1 mg/l, and iridium 0 to 0,3 mg/l.

6. CONDITIONS FOR MEASUREMENT WITH THE PYE UNICAM SP9 SYSTEM

TABLE I-1

Conditions for the measurement of platinum, palladium, rhodium, ruthenium, and iridium with the Pye Unicam SP9 system

Element	Lamp current mA	Slit width nm	Wavelength nm	Background correction
Pt	10	0,2	265,9	Used
Pd	10	0,2	244,8	Used
Rh	10	0,5	343,5	Not used
Ru	10	0,2	349,9	Not used
Ir	15	0,2	208,9(264,0)*	Used

* Note 1

The other measurement conditions are as follows.

Phase 1	{ Drying temperature 95°C Drying time 45 s	Ramp rate 8 (i.e., 5°C/s)
Phase 2	{ Ashing temperature 1000°C Ashing time 30 s	Ramp rate 6 non-linear (i.e., 20°C/s)
Phase 3	{ Atomization temperature 2800°C Atomization time 5 s	Ramp rate (i.e., 1000°C/s)

Aliquot portion of sample 25 µl (transferred to the furnace for measurement)

Argon flow-rate 3 units
Speed of chart recorder 2 mm/min
Amplifier setting for chart recorder 10 mV.

7. PROCEDURE

The procedure up to, and including, the dissolution of the nickel sulphide button¹ is common to all the PGM.

7.1. Fusion

- Transfer 50,0 g of sample (if the PGM content is 1 p.p.m. or less) to a sheet of glazed paper. Add 60,0 g of fused borax, 30,0 g of soda ash (both of assay quality), 32,0 g of nickel carbonate (Note 2), and 12,5 g of powdered sulphur (Note 3). For chromite samples, add 90,0 g of fused borax and 45 g of soda ash. Prepare also at least one sample blank, and include a reference material in each batch of samples (Note 4).
- Roll the mixture from corner to corner of the paper until it is thoroughly mixed, and transfer it to a No. 1 fireclay crucible. Wipe the surface of the glazed paper with a piece of tissue paper, and place this on top of the mixture in the crucible.
- With the aid of furnace tongs, transfer the crucible to a furnace at a temperature of 1000°C. Leave the mixture to fuse for 1¼ hours.
- Remove the crucible and allow the button to cool inside it for approximately 30 minutes. Remove the button by breaking the crucible.

7.2. Dissolution of the Button

- a. Break up the button by pressing it in a hydraulic press. Transfer the pieces to the small bowl of a Siebtechnik mill and grind for 2 minutes.
- b. Brush the sample into a 600 ml squat beaker, add 400 ml of concentrated hydrochloric acid (commercially pure grade), and cover the beaker with a watch-glass. Leave the beaker on a steam-bath at a low temperature for approximately 16 hours. This step is usually carried out overnight.
- c. Remove the beaker from the steam-bath, wash down the lid and sides of the beaker with water, and allow the PGM sulphides to settle and cool for 1 hour.
- d. Bubble hydrogen sulphide into the solution for approximately 1 minute (Note 5).
- e. Filter the solutions under vacuum, using no. 542 Whatman (11 cm) filter papers in Fischer funnels. Wash out the beakers with cold 50 per cent (v/v) hydrochloric acid and wash the papers at least five times with water to remove all traces of nickel. Discard the filtrate.
- f. Pour 10 ml of concentrated hydrochloric acid and 10 ml of hydrogen peroxide (100 vol.) onto the filter paper contained in the funnel, and cover it immediately with a watch-glass.
- g. As the PGM dissolve, collect them in a 100 ml squat beaker. Wash the paper three times with water (Note 6). Discard the filter paper.
- h. Take the solution to moist dryness on a hot-plate and dilute to 5 ml in a volumetric flask.

7.3. Measurement of Platinum, Palladium, Rhodium, Ruthenium, and Iridium

- a. Set up the SP9 system for each element in turn.
- b. Measure each of the calibration standards by using a micropipette to transfer 25 μ l aliquot portions of the standard to the graphite furnace. Make at least two measurements of each standard, and, if the difference between the successive absorbance measurements is greater than 10 per cent, take another measurement.
- c. Measure the blank and the sample solutions in the same way.
- d. Calculate the concentrations of the analytes in the sample from the calibration graph.

$$\text{Analyte in sample, } \mu\text{g/g} = \frac{\text{Concn (from calibration graph)} \times \text{dilution volume}}{\text{Mass taken}}$$

8. NOTES

- (1) At the 208,9 nm line, some samples give severe background effects in the form of a double atomization peak. Should this occur, use the less sensitive 264,0 nm line.
- (2) When a new batch of nickel carbonate is brought into use, carry out several blank determinations to ensure that the PGM are absent.
- (3) If the sulphur content of the samples is higher than 0,5 per cent, decrease the quantity of sulphur added as a flux accordingly. If there is a large amount of excessive sulphur during the fusion, the buttons will be too large and will disintegrate on being cooled.
- (4) It is recommended that the reference material SARM 7 should be included in every batch of samples analysed. Take only 10,0 g of SARM 7 for analysis on the graphite furnace, since the mass is made up with 40,0 g of silica.
- (5) Do not bubble hydrogen sulphide into the solution for too long since this causes sulphates to form in the final solution, which, in turn, might affect measurement of the five PGM.
- (6) Avoid inclusion of the filter paper, which could introduce undesirable organic matter.

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COUNCIL FOR MINERAL TECHNOLOGY

Report M34: The determination, by atomic-absorption spectrophotometry using electrothermal atomization, of platinum, palladium, rhodium, ruthenium, and iridium.

by J. Haines and R.V.D. Robért

Corrigenda

The following amendments should be made to the above report.

- (1) Synopsis, line 10: all the units should be $\mu\text{g}/\text{kg}$.
- (2) Samevatting, lyn 10: al die eenhede moet $\mu\text{g}/\text{kg}$ wees.
- (3) Page 8, Table 7: the unit for limit of determination (the last 4 columns) should be $\mu\text{g}/\text{kg}$.