

REPORT

No. 1555

THE ANALYSIS, BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY, OF MATTE-LEACH RESIDUES

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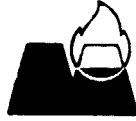
Marinette Dubois

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NATIONAL INSTITUTE FOR METALLURGY
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REPORT ● VERSLAG

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SYNOPSIS

Alternative methods for the analysis of matte-leach residues by atomic absorption spectrophotometry were investigated.

For the determination of the platinum-group metals, gold, and certain of the base metals, a fusion with sodium peroxide, followed by the separation of gold by reverse-phase chromatography and of the platinum-group metals by ion-exchange, is proposed. The noble metals are then determined in a solution that is free of most base metals including the sodium present as a result of the fusion. Copper, nickel, iron, calcium, magnesium, and aluminium can be determined after they have been removed from the ion-exchange column. Arsenic, selenium, tellurium, antimony, bismuth, tin, silver, lead, manganese, zinc, and cobalt can be determined in a separate sample after dissolution by a sealed-tube method. This is also an alternative method for the determination of copper, nickel, and iron. Chromium is determined separately after fusion with sodium peroxide, and silver can also be determined in this way.

The laboratory method for these procedures is given as an appendix.

SAMEVATTING

Alternatiewe metodes vir die ontleding van matteoogresidua's deur atoomabsorptiespektrofotometrie is ondersoek. Vir die bepaling van metaal van die platinumgroep, goud en sekere onedelmetale word 'n smelting met natriumperoksied gebruik deur die skeiding van goud deur omkeertasechromatografie en van die metale van die platinumgroep deur ionuitruiling, voorgesel. Die edelmetale word dan bepaal in 'n oplossing wat vry is van die meeste onedelmetale, insluitende die natrium wat as gevolg van die smelting aanwesig is. Koper, nikkel, yster, kalsium, magnesium en aluminium kan bepaal word nadat hulle uit die ionuitruil kolom verwyder is. Arseen, seleen, telluur, antimoon, bismut, tin, silwer, lood, mangaan, sink en kobalt kan in 'n afsonderlike monster na oplossing volgens 'n verseeldebuismetode bepaal word. Dit is ook 'n alternatiewe metode vir die bepaling van koper, nikkel en yster. Chroom word na die smelting met natriumperoksied afsonderlik bepaal en silwer kan ook op hierdie manier bepaal word.

Die laboratoriummetode vir hierdie prosedures word as 'n aanhangsel aangegee.

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1. INTRODUCTION

The method¹ for the analysis of matte-leach residue (MLR) by atomic-absorption spectrophotometry in which dissolution of the sample is achieved by two sealed-tube attacks suffers from several disadvantages. It is time consuming and prone to errors resulting from the multiple operations, and complete dissolution of the material is not achieved by the sealed-tube attacks alone.

In this report a simpler procedure for the analysis of MLR is proposed. It is a composite method based on a series of techniques that have been described elsewhere. Briefly, the method is as follows:

- (a) fusion of the MLR with sodium peroxide, followed by leaching, acidification, and removal of silica,
- (b) separation of gold on a TBP-treated Porasil C column²,
- (c) separation of the noble metals with BIO RAD AG-50W-X8 cation-exchange resin³,
- (d) stripping of base metals from the resin,
- (e) dissolution of a separate sample with brominated hydrochloric acid and nitric acid in a sealed tube, if base and volatile metals are required urgently⁴,
- (f) fusion of a separate sample for the determination of chromium and silver,
- (g) determination of the noble metals⁵⁻⁷, and
- (h) determination of the base metals^{8,9}.

The disadvantage of a sodium peroxide fusion¹, namely, the introduction of a high salt content, is overcome by the use of a resin separation. The necessity for a separate analysis for chromium arises from the incomplete elution of chromium from cation-exchange resins, and the simultaneous determination of silver avoids the possibility of loss caused by precipitation from weakly acid media.

This report is confined to a description of the tests done on the method for aluminium, calcium, and magnesium, which has not previously been described, and to the presentation and comparison of results obtained for MLR samples by the proposed method and by other methods.

2. EXPERIMENTAL METHOD

2.1. DETERMINATION OF CALCIUM, MAGNESIUM, AND ALUMINIUM

After the resin has been stripped, calcium, magnesium, and aluminium are present, together with the major base-metal components of the MLR (copper, nickel, and iron) and large amounts of sodium from the fusion. It was considered that the poorest MLR likely to be analysed by the proposed method would have copper, nickel, and iron contents of not less than 75 per cent (m/m), and that the lowest level of calcium and magnesium would be 0,1 per cent (m/m). The lowest level of aluminium that could be determined with acceptable accuracy would be 0,5 per cent (m/m). In view of these considerations and the minimum dilutions required by the method, the necessary tests for an adequate assessment of the method were done on synthetic solutions in the presence of copper, nickel, and iron. The solutions for the tests contained sodium chloride and base metals in the highest amounts that are likely to be encountered in samples for which the method is intended. The presence of sodium chloride does not interfere with the measurement of calcium and magnesium, because these metals are present in sufficiently high concentrations and their sensitivity is such that the effect of the salt is overcome by dilution.

From information previously reported^{3,10}, it is known that these cations will be retained on the column in 0,1 M hydrochloric acid and will be stripped off with 6 M hydrochloric acid. The tests were therefore confined to the measurement of interference effects arising from the presence of the various base metals. The results are summarized in Tables 1 and 2.

All trace elements were determined in a hot nitrous oxide-acetylene flame, 1% (m/v) of strontium being added to overcome possible interference from other elements in the determination of calcium and magnesium. In the determination of aluminium, the dilution is such that the aspirated solution has a sodium chloride content (from the fusion salts) of 2 per cent (m/v). This is beneficial in reducing ionization effects¹¹ in the hot nitrous oxide-acetylene flame. In addition, excess iron (to give 5000 p.p.m. in the solution aspirated) was added to overcome interference effects¹¹ in the determination of this element.

It should be noted that many strontium salts are contaminated with calcium. It is therefore recommended that a reagent blank should be taken through the procedure and that a strontium salt of low calcium content should be used.

ANALYSIS OF MATTE-LEACH RESIDUES

TABLE 1

Effect of possible interferences on the measurement of calcium and magnesium when 1% (m/v) strontium is used as the releasing agent

	Possible interference by:	Ca present, p.p.m.			Mg present, p.p.m.		
		1	2	3	1	2	3
Recovery*, %	0.1% NaCl + 40 p.p.m. each of Cu, Ni, Fe	97	102	102	98	100	99
	0.2% NaCl + 80 p.p.m. each of Cu, Ni, Fe	98	100	100	98	100	99
	0.4% NaCl + 160 p.p.m. each of Cu, Ni, Fe	99	102	100	98	100	98
	0.8% NaCl + 320 p.p.m. each of Cu, Ni, Fe	99	99	99	98	99	99
	1.0% NaCl + 400 p.p.m. each of Cu, Ni, Fe	97	99	98	97	99	99

*In this report, the word 'recovery' means the amount of element determined as a percentage of the amount added

TABLE 2

Effect of possible interferences on the measurement of aluminium*

Al concn p.p.m.	Recovery %
10	100
20	100
50	99
100	99

*The matrix was 2% (m/v) NaCl and 5000 p.p.m. of Fe, and the base metals present were Cu, Ni, and Fe (600 p.p.m. each)

2.2. DETERMINATION OF THE PLATINUM-GROUP METALS (PGM)

2.2.1. Conversion of the PGM to the correct Molecular State

If the procedure described in the Appendix is followed, sodium chloride will be present at the stage where the solution is evaporated in the presence of hydrochloric acid, and the need for its presence is clearly shown by the results given in Table 3. When the PGM solutions were evaporated with hydrochloric acid in the absence of sodium chloride, a large portion of ruthenium and a lesser, but measurable, amount of palladium were retained on the resin column in a 0.1 M hydrochloric acid medium. When the solutions were evaporated with hydrochloric acid in the presence of sodium chloride, the recovery of all noble metals in the eluate was good.

In tests 1 to 5, two resin columns containing BIO RAD AG-50W-X8 (50 to 100 mesh) were used, and solutions of the PGM in 0.1 M hydrochloric acid passed through repeatedly. After each solution had been eluted and stripped, the resin was stripped with 1-to-1 hydrochloric acid and regenerated, as described in the Appendix. The eluate from the stripping of the resin in tests 1 and 2 was analysed, and the missing ruthenium and palladium were found, showing that ruthenium and palladium had been retained on the resin. Test 5 was a confirmatory test in which sodium chloride was again absent, and ruthenium and palladium were again lost during the first elution. However, it was not considered necessary to check the eluate from the stripping of the resin for the missing PGM, and, in all the tests where good recoveries were obtained, these eluates were not analysed.

2.2.2. Effect of TBP on the Cation-exchange Resin

Initially the separation of gold by the use of TBP-treated Porasil C was not included in the general scheme of analysis. At that stage satisfactory results were obtained for the PGM when the fine

ANALYSIS OF MATTE-LEACH RESIDUES

TABLE 3

Effect of sodium chloride on the column separation of the PGM

Amounts of PGM added; μg : Pt 5000, Pd 500, Rh 200, Ru 500, Ir 2000

	Amount found, μg							Solution treatment
	Pt	Pd		Rh	Ru		Ir	
	Eluate	Eluate	Resin	Eluate	Eluate	Resin	Eluate	
Test 1	4900	465	25	194	330	165	1980	Repeated evapn with HCl, no NaCl present
	4900	470	17	6	315	192	1980	
Test 2	4900	480	20	198	370	135	2000	
	4900	480	20	198	265	225	1980	
Test 3	4950	495		198	475		2000	
	5000	495		200	500		2000	
Test 4	4950	500		200	490		2000	
	4950	500		198	570		2000	
Test 5	4900	480		196	280		1940	Repeated evapn with HCl, no NaCl present
	4850	480		194	305		1960	

(200 to 400 mesh) BIO RAD resin was used. However, after the gold-separation step had been incorporated, low recoveries were often obtained for the PGM. It was shown that this was caused by TBP in the solution from the gold separation step. The TBP affects the fine resin, thus causing the PGM to be held on the column. Fortunately, the coarse (50 to 100 mesh) resin is not affected in this way. This is shown in Table 4, where PGM solutions after they had been treated with hydrochloric acid and sodium chloride were passed through TBP-treated Porasil C columns (so that TBP would be entrained) and then through columns of coarse or fine resin. In each instance, good recoveries of the added PGM were obtained with the coarse resin, and poor recoveries were obtained for platinum, palladium, ruthenium, and iridium, with the fine resin. The TBP, which is visible as an oily film, was entrained as described, and the procedure described therefore offers a practical situation. Finally the data listed in Table 5 show that, when no TBP is present, good recoveries are obtained with the fine resin, and that significant amounts of platinum, palladium, ruthenium, and iridium are retained on the column when TBP is present. It is interesting to note that, in all the tests (Tables 4 and 5), the recovery of rhodium is not affected by the presence of TBP.

2.3. ANALYSIS OF MLR BY THE PROPOSED AND OTHER METHODS

A sample of MLR was analysed by several different methods and techniques. The results are shown in Table 6. The determination of the noble metals, with the exception of gold, was done on ten separate portions of the sample. The means of the results are shown, and an estimate of the precision of the method is also included. The results for gold are the means of five determinations done subsequently. Although a precise figure for gold is not included for the proposed atomic-absorption method, it should be the same as that quoted for method (d) since the methods are virtually identical up to that stage.

Unfortunately, comparative results were not obtained for all the elements determined. Nevertheless, all the results obtained by the proposed atomic-absorption method are quoted. The results given in Table 6 for platinum, palladium, rhodium, ruthenium, and iridium were obtained when BIO RAD AG-50W-X8 resin of 200 to 400 mesh was used and the gold-separation step with TBP-treated Porasil C was not included in the method. The details of the proposed method are given in the Appendix, and those of the comparative methods referred to as (a), (b), (c), and (d) in Table 6 are very briefly as follows.

TABLE 4

Comparison of the recoveries of PGM in the eluate from coarse and fine resin in the presence of TRP

Amounts of PGM added, μg : Pt 5000, Pd 500, Rh 200, Ru 500, Ir 2000

Amount found in eluate, μg									
Pt		Pd		Rh		Ru		Ir	
C*	F†	C	F	C	F	C	F	C	F
4950	2300	495	380	198	194	475	500	2000	1760
5000	3700	495	430	200	188	500	285	2000	1780
4950	2000	500	350	200	198	490	375	2000	1800
4950	2000	500	430	198	198	490	430	2000	1900

*Coarse (50 to 100 mesh) BIO RAD AG-50W-X8 cation-exchange resin

†Fine (200 to 400 mesh) BIO RAD AG-50W-X8 cation-exchange resin

TABLE 5

Comparison of the recoveries of PGM in the eluate from fine resin* in the presence and absence of TBP

Amount found in eluate, μg					
	Pt	Pd	Rh	Ru	Ir
No TBP	5000	485	200	480	1960
TBP present	3300	440	198	410	1780

*200 to 400 mesh BIO RAD AG-50W-X8 cation-exchange resin

TABLE 6

Comparison of results obtained by the proposed method with those obtained by other methods

Element determined	Proposed method		Method (a)	Method (b)	Method (c)	Method (d)	
	%	Precision C of V, %	%	%	%	%	Precision C of V, %
Pt	18.18	1.0	18.06	18.37		18.64	0.6
Pd	8.06	1.0	7.98	8.11		7.88	0.9
Rh	0.81	0.77	0.88			0.89	1.2
Ru	1.73	2.0	1.88	1.66			
Ir	0.19	4.3	0.19			0.26	2.6
Au	1.32		1.40	1.36		1.39	0.95
Os			0.19				
Ag	0.149		0.13				
Ca	0.45				0.42		
Mg	0.84				1.11		
Al	1.94				1.74		
Fe	6.32	1.76			7.6		
Ni	5.01	0.72			5.04		
Cu	5.84	0.80			5.85		
Co	0.17	1.1					
Bi	0.054	1.9					
Sb	0.054	3.6					
As	0.97	1.9					
Se	1.98	3.1					
Te	0.36	2.3					
Cr	3.17				2.87		

Method (a) is a fire-assay procedure, nickel sulphide being used as the collector^{1,2}. The noble metals were separated from the nickel sulphide by dissolution of the latter with hydrochloric acid. The insoluble residue containing the PGM, gold, and silver was dissolved, and the PGM (excluding osmium) and silver were determined by atomic-absorption spectrophotometry. Osmium was separated by distillation and determined by a spectrophotometric method^{1,3}.

Method (b) involved classical separation of the noble metals and gravimetric determinations. After dissolution of the MLR by a combination of acid attack and sodium peroxide fusion, ruthenium was removed by distillation, reduced with hydrogen, and determined gravimetrically. Gold was separated by a ferrous sulphate precipitation, purified by a second precipitation step with sodium nitrate, and finally determined gravimetrically after ignition. After the removal of base metals with BIO RAD AG-50W-X8 cation-exchange resin, palladium was precipitated and separated with dimethylglyoxime, and was then reduced with hydrogen and determined gravimetrically. Rhodium and iridium were separated together by a bromate hydrolysis, but were not determined. Platinum was precipitated with hydrazine hydrate and was determined gravimetrically after reduction with hydrogen.

Method (c) refers to standard volumetric procedures for the determination of copper, iron, aluminium, and chromium, and gravimetric procedures for the determination of calcium, magnesium, and nickel after the noble metals had been removed with hydrogen sulphide.

Method (d) is the combined use of TBP-treated Porasil C, BIO RAD AG-50W-X8 resin, and cellulose-column separations of the noble metals³. Platinum and palladium were determined gravimetrically, and gold, rhodium, and iridium were determined by atomic-absorption spectrophotometry.

The agreement between the various methods for the determination of the noble metals is acceptable. The precision for iridium by the proposed method is somewhat poor owing to the low concentration levels for this element and its poor sensitivity by AAS. The agreement between the proposed method and method (c) for calcium, nickel, and copper is good, but that for magnesium, aluminium, iron, and chromium is poor. The results shown in Table 6 for nickel, copper, and iron were obtained after the sealed-tube dissolution procedure. (see Section 5 of the Appendix), and there is no reason to suspect that iron is not dissolved. However, although the reason is not clear, it appears that the iron result quoted is low, since a subsequent analysis (method used for chromium) yielded a result of 7.43 per cent for iron, which is in better agreement with the value obtained by the volumetric method. The reason for the discrepancy for magnesium, aluminium, and chromium is not obvious. Little can be said about the other base metals determined because no comparative results were obtained.

2.4. COMPARISON OF RESULTS WITH THOSE OBTAINED BY AN INDEPENDENT LABORATORY

Two samples of MLR, designated A and B, were analysed for noble-metal content by the proposed method at NIM and by an independent laboratory. The methods used by the independent laboratory are not known. The results are shown in Table 7, where it can be seen that the agreement is reasonably good.

TABLE 7

Comparison of results with those obtained by an independent laboratory

Element	Content, %			
	Sample A		Sample B	
	Proposed method	Indep. lab.	Proposed method	Indep. lab.
Pt	18.26	18.64	14.24	14.50
Pd	7.82	7.91	5.98	5.89
Rh	0.82	0.87	0.61	0.62
Ru	1.80	1.67	1.33	1.23
Ir	0.19	0.23	0.17	0.20
Au	1.28	1.51	1.16	1.15

3. DISCUSSION

The method as described in the Appendix for the analysis of matte-leach residues evolved during the routine analysis of many samples. With the exception of a few elements that are not suitable for atomic-absorption measurements, a complete analysis can be made by this method. As far as can be ascertained, the results and precision are acceptable.

Because of the problems encountered with the fine (200 to 400 mesh) BIO RAD resin and those caused by TBP, it is recommended that the coarser (50 to 100 mesh) resin should be used. Why the fine resin is affected, and not the coarse resin, is not yet understood.

Dowex 50-X8 resin has similar properties to those of the BIO RAD resin⁵, and, although the latter are purer, for this application there is no obvious reason why Dowex cannot be used. Preliminary tests with synthetic solutions and the analysis of check samples indicate that Dowex 50-X8 is equal to the BIO RAD resin.

Certain of the base metals, e.g., copper, nickel, and iron, can be determined either after being stripped from the resin or after dissolution of the MLR by the sealed-tube method. (These metals could also be determined along with chromium after a sodium peroxide fusion.) The choice of method for the base-metal determination will depend largely on the requirements of the analysis. If, for example, only copper, nickel, and iron are requested, as often happens, then the base metals would be determined after being stripped from the resin column and the sealed-tube method would not be used. If, however, the base metals, including volatile elements such as arsenic and selenium, were required very urgently, then the sealed-tube attack on a separate sample would be used. If only copper, nickel, and iron were required urgently, a simple fusion of a separate sample with sodium peroxide, as in the method for chromium, could be used.

Although this procedure has not yet been tested, it should be possible to determine zinc, lead, cobalt, and manganese in the eluate containing the base metals stripped from the BIO RAD resin. The distribution coefficients are favourable¹⁰. Provided that tin remains as the stannic ion, it, too, could be separated from the PGM in 0.1 M hydrochloric acid and subsequently eluted. Depending on the final dilution required for the determination of these elements, it may be necessary to match the calibration standards with respect to sodium chloride content.

A serious interference that may be encountered in the determination of the noble metals with the proposed atomic-absorption method would be that due to the presence of sulphate ions¹⁴. For this reason it is recommended that the sample should be roasted to remove as much sulphur as possible. Sufficient dilution will also remove this interference (see Appendix). However, this simple expedient cannot always be employed satisfactorily, e.g., where low concentration levels of measured element, or poor sensitivity (e.g., iridium), are encountered. Other means of overcoming this interference can be used, namely, use of lanthanum instead of uranium as a releasing agent¹⁴, and the removal of sulphate ions by precipitation¹⁵ as BaSO₄.

It is estimated that the analysis of ten samples for the determination of the noble metals and the base metals (using the sealed-tube method for base metals) would take an experienced analyst approximately five days to complete. This is more rapid than the classical methods for the determination of only the noble metals. By the proposed method the noble metals can be determined in three days. By fire assay (nickel sulphide collection)¹², however, the noble metals can be determined in two days. So, although the proposed method for noble metals is still not as rapid as the nickel sulphide fire-assay method, it does afford an alternative method having fairly general application.

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APPENDIX

THE ANALYSIS, BY ATOMIC-ABSORPTION SPECTROPHOTOMETRY,
OF MATTE-LEACH RESIDUES (LABORATORY METHOD NO. 78/16)

1. APPLICATION

The application of the method to noble metals and to base metals is described separately.

1.1. NOBLE METALS

The method was developed for the determination of the noble metals (platinum, palladium, rhodium, ruthenium, iridium, and gold) in matte-leach residues in which the total noble-metal content is more than 0.5 per cent (m/m). However, the method has more general applicability and can be used wherever the noble-metal content is sufficiently high and fusion is necessary for dissolution of a sample, or where base metals must be removed prior to measurement. Because sulphate interferes with the determination of the noble metals, the amount of sulphate ion in the solution for measurement should be known. For control of this interference, see step 18 of Section 3.3.

1.2. BASE METALS

In matte-leach residues, the major base metals are copper, nickel, and iron, although calcium, magnesium, and aluminium may also be present at relatively high levels of concentration. After these base metals have been eluted from the column, little difficulty should be encountered in their determination, with the possible exception of aluminium. Because the sensitivity for aluminium is poor, aluminium contents of less than 0.5 per cent (m/m) in the MLR may yield results of somewhat poor accuracy. The minor base metals (cobalt, arsenic, selenium, tellurium, and chromium) are usually present in sufficient quantity - 0.1 to 2 per cent (m/m) - to be determined satisfactorily. Bismuth and antimony may be present at lower levels (less than 500 p.p.m.), but, unless present in trace amounts (less than 50 p.p.m. for bismuth and less than 200 p.p.m. for antimony), they can still be determined with acceptable accuracy. Silver can be determined satisfactorily if more than 25 p.p.m. is present, although lower levels can be determined if a lower accuracy is acceptable.

2. DETERMINATION OF NOBLE METALS

2.1. APPARATUS AND REAGENTS

(1) BIO RAD Columns

These are glass columns 40 cm in length with a diameter of 2.5 cm. They should have a ground-glass joint at the top to take a 500 ml reservoir. The reservoir and column should be fitted with taps, and the column should have a sintered-glass disc at the bottom to hold the column of resin. The column is filled with prepared resin to a height of 25 cm.

(2) TBP-treated Porasil C Columns

These are glass columns 30 cm in length with a diameter of 1.2 cm. They should be fitted with taps and sintered-glass discs. Each column should contain 1.5 g of prepared TBP-treated Porasil C.

(3) Sodium Peroxide

A.R. grade.

(4) Hydrochloric Acid, 10% (v/v)

Dilute 100 ml of concentrated hydrochloric acid to 1 litre with water.

(5) Hydrochloric Acid, 12 M

A.R. grade.

(6) Hydrochloric Acid, 40% (v/v)

Dilute 400 ml of concentrated hydrochloric acid to 1 litre with water.

(7) Hydrochloric Acid, 0.1 M

Dilute 8.4 ml of 12 M hydrochloric acid to 1 litre with water.

(8) Hydrofluoric Acid, 48%

A.R. grade.

(9) Nitric Acid, 65%

A.R. grade.

(10) Uranium Solution, 250 g/l

Dissolve 29.5 g of pure U_3O_8 in 20 ml of nitric acid, and dilute to 100 ml with water.

(11) Cation-exchange Resin

Use BIORAD AG-50W-X8, mesh size 50 to 100, obtainable from BIORAD Laboratories, Richmond, California. New resin should be cleaned and conditioned by being heated gently in a beaker with hydrochloric acid diluted 1 to 1. The excess acid should then be removed by repeated decantation and washing with water until the resin is neutral to litmus paper.

(12) TBP-treated Porasil C

Use Porasil C, size 100 to 150 mesh, obtainable from Waters Associates, Inc., Massachusetts. Wash 15 g of Porasil C with hydrochloric acid, and then with water to remove the acid. Dry, and add 5 g of TBP dissolved in chloroform. Stir the slurry until most of the chloroform has evaporated. Dry the material in an air-oven at 75 °C. To 1.5 g of the TBP-treated Porasil C in a small beaker, add water to form a slurry, and transfer the slurry to the column. Drain the surplus water, and condition by washing with 10 ml of 0.1 M hydrochloric acid.

2.2. STANDARD SOLUTIONS

(1) Stock Solutions

Stock solutions of platinum, palladium, and gold are made by dissolution of the pure metal in aqua regia and are treated as described in Laboratory Method No. 6¹. The solutions for rhodium, ruthenium, and iridium are made from the pure metals dissolved by chlorination in sealed-tubes².

(2) Combined Standard Solution

From the stock solutions, prepare 100 ml of a combined noble-metal solution to contain the following in a 10% (v/v) hydrochloric acid medium: platinum 1000 p.p.m.; palladium, rhodium, and gold 100 p.p.m. each; ruthenium 400 p.p.m.; and iridium 500 p.p.m.

(3) Calibration Standards

Accurately transfer 0, 1, 2, 3, 4, 6, 10, 12, 15, and 20 millilitres of the combined standard solution to a set of 100 ml volumetric flasks, add 4 ml of uranium solution (uranium 250 mg/ml), and dilute to the mark with 40% (v/v) hydrochloric acid. The calibration range is summarized in Table 1.

TABLE 1

Noble-metal contents of the calibration standards

Metal	Concentration, p.p.m.									
	0	10	20	30	40	60	100	120	150	200
Pt	0	10	20	30	40	60	100	120	150	200
Pd	0	1	2	3	4	6	10	12	15	20
Rh	0	1	2	3	4	6	10	12	15	20
Ru	0	4	8	12	16	24	40	48	60	80
Ir	0	5	10	15	20	30	50	60	75	100
Au	0	1	2	3	4	6	10	12	15	20

2.3. PROCEDURE

- Accurately measure out two 0.5 g portions of MLR into 20 ml zirconium dishes. (For duplicate analyses, measure out three portions.)
- Place the dishes in a muffle furnace, raise the temperature to 700 °C, and roast for 1 hour. The sample should be stirred every 15 minutes.
- Remove the dishes, cool, and submit one sample for chemical determination of the total sulphate content. To the other sample, add 3 g of sodium peroxide. Mix well, and sinter over a low flame. Raise the temperature until the sample is fluid, and fuse at a dull red heat for approximately 1½ minutes.
- Cool, and leach the melt with 40 ml of water in a 125 ml squat beaker.
- Add 20 ml of concentrated hydrochloric acid. Remove the zirconium dish, and rinse with water.
- Evaporate the solution to dryness, and then take to dryness twice with 5 ml of concentrated hydrochloric acid. Bake on a hot-plate at 110 °C for 1 hour to dehydrate the silica. (The initial evaporation may be done overnight on a steam-bath.)
- Add 50 ml of 0.1 M hydrochloric acid and heat to dissolve the salts. If necessary, add a few drops of hydrogen peroxide to aid dissolution.

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- h. Filter through a Whatman no. 40 filter paper to remove the silica. Wash thoroughly with hot 0.1 M hydrochloric acid until the paper and residue are free of colour. If the residue is small and clean, proceed immediately to step i. If the silica content is very high, or if the silica is coloured even after thorough washing, sluice the residue into a Teflon beaker. Add 10 ml of hydrofluoric acid and evaporate to dryness to remove the silica. Add 10 ml of concentrated hydrochloric acid and evaporate to dryness. Repeat this step twice more. Finally, add 25 ml of 0.1 M hydrochloric acid, warming to dissolve the salts, and then add to the original filtrate and rinse the beaker with 0.1 M hydrochloric acid.
- i. The solution before passing through the columns should be approximately 200 ml in volume, and its hydrochloric acid concentration should be 0.1 M. Adjust if necessary, and pass the solution through the TBP-treated Porasil C column at maximum elution speed to remove the gold. Rinse the beaker with 20 ml of 0.1 M hydrochloric acid. Rinse the column with a further 5 ml of 0.1 M hydrochloric acid.
- j. Elute the gold with 25 ml of concentrated nitric acid.
- k. Evaporate the gold eluate to near dryness and dilute to a suitable volume with 40 % hydrochloric acid. Do not allow the solution to go to dryness because gold may then be lost. Because of the presence of TBP, it may be necessary to use a rubber 'policeman' to help wash gold from the beaker. (A volume of 25 ml, from which further dilutions can be made, will usually be suitable.)
- l. Pass the eluate from the TBP-treated Porasil C column, which contains the noble and base metals, through the BIO RAD AG-50W-X8 ion-exchange column at a flowrate of approximately one drop per second. Collect the eluate in a 600 ml beaker.
- m. Wash the noble metals through the column by rinsing the beaker with 20 ml of 0.1 M hydrochloric acid and then with 200 ml of 0.1 M hydrochloric acid placed in the reservoir.
- n. Evaporate the eluate down to a low volume (ca 20 ml) and transfer it to a 50 ml squat beaker, rinsing with 0.1 M hydrochloric acid.
- o. Evaporate to incipient dryness, add 10 ml of 12 M hydrochloric acid, and warm to dissolve the salts.
- p. Cool and transfer to a 25 ml volumetric flask, rinse the beaker with water, add 1 ml of uranium solution, and dilute to the mark with water.
- q. Take appropriate aliquot portions, and make further suitable dilutions where necessary (adding uranium solution) for the measurement of the noble metals (see step r). Measurements of the noble metals, including gold, are made in 40 % (v/v) hydrochloric acid and 1 % (m/v) uranium media^{3,4}. See Table 3 for conditions.
- r. From the chemical analysis of the MLR for sulphate content, calculate the amount of sulphate present in the solution from step p. Then calculate the dilution required either to reduce the sulphate content to an acceptable level for the corresponding PGM level or simply to lower the PGM level, noting that there is greater tolerance towards interference by sulphate ions at lower levels of PGM concentration. Choose whichever dilution results in the higher PGM level for better precision. See Table 2. Sulphate will not be present in the gold solution.
- Examples:*
- (a) Pt 40 p.p.m., SO₄²⁻ 4 %. Dilute twofold to give 20 p.p.m. of Pt in 2 % SO₄²⁻ rather than diluting twentyfold to give 0.2 % SO₄²⁻, where Pt would be 2 p.p.m.
- (b) Pt 100 p.p.m., SO₄²⁻ 0.4 %. Dilute twofold to give 0.2 % SO₄²⁻, where Pt would be 50 p.p.m., rather than diluting fivefold to give 20 p.p.m. of Pt.
- In most analyses of MLR the level of PGM is sufficiently high for the interference by sulphate ions to be automatically eliminated by the necessary dilution. An exception may occur in the determination of iridium.
- s. Use the instrumental settings and flame types shown in Table 3.

3. DETERMINATION OF BASE METALS RETAINED ON BIO RAD COLUMN

Several base metals retained on the column in step m of Section 3.3 can be determined. The measurement of the following elements has been confirmed: copper, nickel, iron, aluminium, calcium, and magnesium. Although not confirmed by tests, it should be possible to determine cobalt, manganese, zinc, and lead since these elements are also held on the column with 0.1 M hydrochloric acid and eluted with 1-to-1 hydrochloric acid⁵. (Lead should not be so high as to precipitate as PbCl₂ in 0.1 M hydrochloric acid.)

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TABLE 2

Interference by sulphate ions when uranium is used as the releasing agent in 40 % (v/v) hydrochloric acid

Element measured	Concentration of SO ₄ ²⁻ below which no interference occurs in the PGM concn range shown		Concentration range of PGM in which no interference of SO ₄ ²⁻ occurs - tested up to 4 % (m/v) of SO ₄ ²⁻ p.p.m.
	SO ₄ ²⁻ concn % (m/v)	PGM concn p.p.m.	
Pt	0.2	0 to 100	0 to 20
Pd	1.0	0 to 10	*
Rh	0.2	0 to 10	0 to 2
Ru	0.2	0 to 50	0 to 10
Ir	0.2	0 to 50	0 to 5
Au	2.0	0 to 10	0 to 3

*There is slight interference over the whole Pd concentration range, and the SO₄²⁻ concentration should therefore be kept below 1 % (m/v)

TABLE 3

Instrumental parameters for the measurement of the noble metals

Element	Wavelength A	Slit μm	Lamp current mA	Flame
Pt	2659.5	50	10	AAF lean
Pd	2447.9	50	5	AAF lean
Rh	3434.9	100	5	AAF medium
Ru	3498.9	50	10	AAF rich
Ir	2639.7	100	20	AAF rich
Au	2428.0	100	4	AAF lean

AAF = air-acetylene flame

The following additional reagents are required:

- (1) *Strontium Nitrate*
A.R. grade. Use salt of low calcium content.
 - (2) *Potassium Nitrate*
A.R. grade
 - (3) *Sodium Chloride*
A.R. grade
 - (4) *Ferric Chloride Solution 10 % (m/v)*
Dissolve 48 g of A.R.-grade FeCl₃ · 6H₂O in 10 % (v/v) hydrochloric acid and dilute to 100 ml with 10 % (v/v) hydrochloric acid.
The following procedure should be followed.
- a. Strip the base metals from the BIO RAD column by eluting with 400 ml of 1-to-1 hydrochloric acid. Then wash the resin out into a 600 ml beaker, and neutralize by repeated decantations with water until the resin is free of acid. Test with litmus paper. Repack the columns for future use.

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- b. Evaporate the stripping solution down to incipient dryness and then dilute to 200 ml with 5% (v/v) hydrochloric acid. The sodium chloride concentration of the solution will be approximately 2.2% (m/v) owing to the fusion salts.
- c. Take suitable aliquot portions for the determinations of nickel and iron, dilute to volume with 4% (v/v) nitric acid, and add potassium nitrate to give 1% (m/v) in the solution for measurement. Measure against suitable standards using the nitrous oxide-acetylene flame (see Table 4).
- d. Take suitable aliquot portions for the determination of copper and dilute them to volume with 4% (v/v) nitric acid. Measure against suitable standards using the air-acetylene flame (Table 4).
- e. Take suitable aliquot portions for the determination of aluminium, diluting with 5% (v/v) hydrochloric acid and adding iron to give 5000 p.p.m., and sodium chloride to give 2% (m/v) in the solution for measurement. (The iron already present, unless above 10% (m/m) in the MLR, can be disregarded; otherwise, allowance should be made for this amount of iron.) Measure against suitable standards in 2% (m/v) sodium chloride solution containing 5000 p.p.m. of iron, using the nitrous oxide-acetylene flame (Table 4).
- f. Take suitable aliquot portions for the determination of calcium and magnesium, dilute with 5% (v/v) hydrochloric acid, and add strontium nitrate to give 1% (m/v) of strontium in the solution for measurement. (Large dilutions are generally required, and the calibration standards need not be matched for sodium chloride content.) Use the nitrous oxide-acetylene flame for measurement (Table 4).

TABLE 4

Instrumental parameters for the measurement of base metals

Element	Wavelength Å	Slit µm	Lamp current mA	Flame*	Medium	Calibration range p.p.m.
Ni	2320	50	8	NOA	4% HNO ₃ + 1% KNO ₃	0 to 50
Fe	2483	50	5	NOA		0 to 50
Mn	2795	50	5	NOA		0 to 10
Cr	3579	100	5	NOA		0 to 20
Co	2407	25	5	NOA		0 to 20
Al	3093	50	10	NOA		5% HCl + 2% NaCl + 500 p.p.m. Fe
Ca	4227	100	4	NOA	5% HCl + 1% Sr	0 to 5
Mg	2852	100	3	NOA		0 to 5
As†	1937	300	7	NOA	10% HCl	0 to 100
Se†	1961	300	10	AA		0 to 50
Te†	2143	100	8	AA		0 to 50
Sb†	2176	100	10	AA		0 to 50
Bi†	2231	50	8	AA		0 to 20
Sn†	2355	100	8	NOA		0 to 100
Ag	3281	50	4	AA		0 to 5
Pb	2170	300	6	AA		10% HCl or 4% HNO ₃
Cu	3248	50	3	AA	4% HNO ₃	0 to 10
Zn†	2139	100	6	NOA		0 to 5

* NOA nitrous oxide-acetylene

AA air-acetylene

† Non-atomic-absorption corrections required

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4. DETERMINATION OF BASE METALS BY SEALED-TUBE DISSOLUTION

The following base metals can be determined by this procedure: selenium, tellurium, arsenic, antimony, bismuth, tin, silver, lead, copper, nickel, iron, manganese, zinc, and cobalt. Although copper, nickel, and iron can be determined on the strip solution from the BIO RAD column, selenium, tellurium, arsenic, antimony, bismuth, and tin should be determined after a sealed-tube attack. (Silver can be determined by this procedure if the method for chromium is not used.) Some of these elements form volatile compounds or are not suitable for ion-exchange separation. The large amount of noble metals present in MLR materials precludes the determination of aluminium, calcium, and magnesium unless the levels of the latter are sufficiently high as to require a relatively large dilution that will minimize the interfering effects.

The following procedure should be followed.

- a. to h. Follow the dissolution procedure described in Laboratory Method No. Pt 78/2⁶. For MLR samples, only 0.5 g of material should be taken, and not 1 g as mentioned there.
- i. Gently evaporate the combined filtrates from steps g and h to incipient dryness on a steam-bath, and then dilute to 25 ml with 10% (v/v) hydrochloric acid solution.
- j. Take suitable aliquot portions for the determination of the required base metals, and dilute with the appropriate medium (Table 4).
- k. Measure against suitable standards (see Table 6).

5. DETERMINATION OF CHROMIUM AND SILVER

Because chromium is not well separated on the resin column and is not always completely dissolved by the sealed-tube attack, and because there is a possibility of loss of silver chloride in the dilute acid required for ion exchange separation, these metals are determined separately by the following procedure.

- a. Fuse 0.5 g of MLR with 3 g of sodium peroxide in a zirconium crucible.
- b. Leach with water and then acidify with 25 ml of concentrated hydrochloric acid.
- c. Dilute to 100 ml with water in a volumetric flask.
- d. For chromium, take a suitable aliquot portion and dilute with 4% (v/v) nitric acid and 1% (m/v) potassium nitrate.
- e. For silver, take a suitable aliquot portion and dilute with 10% (v/v) hydrochloric acid, matching for sodium chloride content if this is above 1% (m/v).

6. PREPARATION OF CALIBRATION STANDARDS FOR DETERMINATIONS OF BASE METALS

6.1. STOCK SOLUTIONS

All stock solutions are made up to contain 1 mg of the metal per millilitre as described in the Varian Techtron Handbook 'Analytical methods for flame spectroscopy'.

6.2. WORKING STANDARD SOLUTIONS

The stock solutions are diluted to give working standard solutions having the concentrations shown in Table 5. Approximately 200 ml of working solution is required and should be in the acid medium shown.

TABLE 5

Working standard solutions

Element	Concentration µg/l	Acid medium (v/v)
Ni, Fe	100	4% HNO ₃
Se, Te, Sb	100	10% HCl
Mn, Cr, Co, Pb, Cu	50	4% HNO ₃
Bi	50	10% HCl
Ca, Mg	20	5% HCl
Zn, Ag	20	4% HNO ₃
As, Al, Sn	Use stock solutions	

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6.3. CALIBRATION STANDARDS

Aliquot portions of the working standard solutions are transferred to 100 ml volumetric flasks. The volumes required are summarized in Table 6, and the media with which the standards should be diluted are shown in Table 4.

TABLE 6

Volume and concentration of the calibration standards

Element	Aliquot volume, ml	Concentration, p.p.m.
Ni, Fe, Se, Te, Si	0, 5, 10, 20, 30, 40, 50	0, 5, 10, 20, 30, 40, 50
Cr, Co, Pb, Bi	0, 4, 8, 12, 20, 30, 40	0, 2, 4, 6, 10, 15, 20
Mn, Cu	0, 2, 4, 6, 10, 15, 20	0, 1, 2, 3, 5, 7.5, 10
Ca, Mg, Ag, Zn	0, 2.5, 5, 10, 15, 20, 25	0, 0.5, 1, 2, 3, 4, 5
V, Al, Sn	0, 1, 2, 3, 6, 8, 10	0, 10, 20, 30, 60, 80, 100

7. REFERENCES

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