

**REPORT**

No. 1783

**THE SPECTROGRAPHIC DETERMINATION  
OF MINOR AND TRACE ELEMENTS IN  
COPPER, LEAD, AND ZINC CONCENTRATES**

**Director of Division** E.W. Steele

**Investigators** R.L. Breckearidge  
G.M. Russell  
A.E. Watson

**Date** 19th February, 1976

**Project** 10274

**Project Report No.** 1

**NATIONAL  
INSTITUTE  
for  
METALLURGY**



**NATIONAL INSTITUTE FOR METALLURGY**  
**NATIONALE INSTITUUT VIR METALLURGIE**

**REPORT ● VERSLAG**

**No. 1783**

**THE SPECTROGRAPHIC DETERMINATION OF MINOR AND TRACE  
ELEMENTS IN COPPER, LEAD, AND ZINC CONCENTRATES**

**19th February, 1976**

**Investigators: R.L. Breckenridge  
G.M. Russell  
A.E. Watson**

**ISBN 0 86999 236 8**

## SYNOPSIS

This report deals with the development of a method for the determination, by an emission-spectrographic technique, of magnesium, manganese, aluminium, silver, calcium, chromium, cobalt, titanium, antimony, cadmium, molybdenum, zirconium, nickel, boron, vanadium, arsenic, beryllium, tin, germanium, and bismuth in copper, lead, and zinc sulphide concentrates.

The method involves the preparation of complex standards in which the volatile elements arsenic, antimony, cadmium, tin, and bismuth are incorporated as sulphide compounds at temperatures of 800 °C in evacuated silica tubes together with a synthetic sulphide matrix. These standards are then mixed with the other minor and trace elements to form composite standards. The conditions for excitation with a direct-current arc, and the analytical lines for the elements and internal standards, are given. The procedure is rapid and convenient, and involves the minimum of sample preparation. The accuracy is about 10 per cent, and the method has a coefficient of variation for the various elements of between 2 and 13 per cent.

## SAMEVATTING

Hierdie verslag handel oor die ontwikkeling van 'n metode vir die bepaling van magnesium, mangaan, aluminium, silwer, kalsium, chroom, kobalt, titaan, antimoon, kadmium, molibdeen, sirkonium, nikkell, boor, vanadium, arseen, berillium, tin, germanium en bismut in koper-, lood- en sink-sulfiedkonsentrate deur 'n emissiespektrografiese tegniek.

Die metodes behels die bereiding van komplekse standaarde waarby die vlugtige elemente arseen, antimoon, kadmium, tin en bismut as sulfiedverbindings ingesluit is, by 'n temperatuur van 800 °C in geëvakueerde silikabuise saam met 'n sintetiese sulfiedmatriks. Hierdie standaarde word dan met die ander elemente met 'n laer konsentrasie en spoorelemente gemeng om saamgestelde standaarde te vorm. Die voorwaardes vir opwekking met 'n geïykstroomboog en die analitiese lyne vir die elemente en interne standaarde word gegee. Die prosedure is vinnig en gerieflik en vereis die minimum monsterbereiding. Die akkuraatheid is ongeveer 10 persent en die metode het 'n variasiekoëffisiënt van tussen 2 en 13 persent vir die verskillende elemente.

## CONTENTS

1.	INTRODUCTION	1
2.	EXPERIMENTAL METHODS	1
	2.1. PREPARATION OF TRACE-ELEMENT MIXTURES	1
	2.2. PREPARATION OF CALIBRATION STANDARDS	2
	2.3. BUFFER	2
	2.4. INTERNAL STANDARDS	2
	2.5. CONDITIONS FOR EXCITATION	2
3.	ACCURACY AND PRECISION	2
4.	MATRIX VARIATIONS	3
5.	DISCUSSION	3
6.	CONCLUSIONS	3
7.	REFERENCES	4
Table 1	Composition of the samples	5
Table 2	Composition of the copper, lead, and zinc matrices	5
Table 3	Composition of the trace-element mixtures	6
Table 4	Values obtained by various techniques for sulphide materials	7
Table 5	Precision of the method	8
Table 6	Composition of the matrices of the samples and standards analysed	8
Table 7	Comparison of results obtained on mixed concentrates with calculated values	9
APPENDIX	THE SPECTROGRAPHIC DETERMINATION OF MINOR AND TRACE ELEMENTS IN COPPER, LEAD, AND ZINC CONCENTRATES (LABORATORY METHOD NO. 16/20)	10
Table I-1	Conditions for the excitation of copper, lead, and zinc concentrates	13
Table I-2	Composition of the copper, lead, and zinc matrix	13
Table I-3	Composition of trace-element mixtures	14
Table I-4	Calibration standards to be used	15
Table I-5	Composition of calibration standards	15
Table I-6	Analytical lines	16
Figure I-1	Silica-glass tubes for sintering of volatile elements	17

## 1. INTRODUCTION

There are very few publications dealing with the simultaneous analysis by instrumental techniques of sulphide concentrates for trace elements, and these are generally confined to the determination of a few specific elements. As a result of the recent exploitation of large sulphide ore-bodies, it became necessary to develop a rapid technique for the analysis of concentrates that would indicate whether they would meet the smelting requirements. An emission-spectrographic technique appeared to hold the most promise because of its inherent sensitivity, its ability to analyse simultaneously for many elements, and its need for the minimum of sample preparation. A disadvantage is the relatively poor precision associated with the analysis for trace elements by direct-current arc, but this decreases in importance with decreasing concentration of the elements.

As the spectrographic technique is essentially a comparative method, the first requirement is the preparation of a reliable set of standards for calibration purposes. It is generally agreed that, if a spectrochemical method is to achieve acceptable accuracy, the standards and samples should be as closely matched in the composition of their major elements and their physical states as is conveniently possible. Because the concentrates for analysis are high in sulphur, the matrices of the calibration standards should be prepared as the sulphides of the major elements, which are copper, lead, zinc, and iron. The exact chemical composition of the sulphide used in the preparation of the matrix should be known, and closely controlled precipitation techniques must be used<sup>1,2</sup> in conjunction with materials of the highest purity available if contamination is to be avoided.

The concentrates used in this work had the compositions shown in Table 1. Because of the big differences in composition, it was concluded that calibrations should be effected for each type of concentrate, starting with the copper concentrate, after which investigations relating to the other two types of concentrates would be undertaken. For each concentrate, the matrix was prepared to match the average composition of the test samples.

## 2. EXPERIMENTAL METHODS

A conventional calibration based on the addition of trace elements as oxides to a sulphide matrix was examined first. The synthetic matrix of the copper concentrate was prepared by thorough mixing of the copper, lead, zinc, iron, and silica compounds in the concentrations shown in Table 2.

A set of standards was prepared by the addition to this synthetic sulphide matrix of oxide compounds of the minor and trace elements of interest, and dilution with the pure matrix. Under conditions similar to those finally adopted and with germanium as the internal standard, it was found that the spectrographic determination of elements of medium volatility and of the refractory elements was generally satisfactory. However, that of the volatile elements (namely, cadmium, bismuth, arsenic, antimony, and tin) was unsatisfactory, giving values that were equivalent to about half those obtained for natural standard samples by other techniques. This indicated that synthetic oxide mixtures do not necessarily behave in the arc in the same way as do natural materials in which the elements are present as sulphides that are possibly incorporated within the lattice structure of the basic mineral<sup>3,4</sup>.

The oxides of cadmium, bismuth, antimony, arsenic, and tin, together with the matrix were placed in a sealed quartz-glass tube under vacuum at 800°C according to the technique described by Mays *et al.*<sup>3</sup>. This procedure was introduced as an attempt to overcome the uncharacteristic behaviour of these volatile elements. However, because of the formation of sulphur dioxide, the tubes were under considerable pressure after the heat treatment, and a portion of the contents was ejected when the tube was opened.

It was therefore decided to prepare the volatile elements as their sulphide compounds, and subsequently to incorporate them with a matrix of sulphide material. The various sulphide compounds of cadmium, arsenic, antimony, tin, and bismuth were prepared in the same way as for the matrix elements<sup>1,2</sup>, and the concentrations of the elements were determined by atomic-absorption spectrophotometry.

### 2.1. PREPARATION OF TRACE-ELEMENT MIXTURES

The compositions of these standards in their respective matrices are given in Table 3. The standards were prepared by the addition of the elements concerned as oxides or sulphides to the

## SPECTROGRAPHIC ANALYSIS OF CONCENTRATES

copper, lead, or zinc matrices. The constituents were thoroughly mixed by being ground in an agate mortar under acetone, after which they were dried and shaken mechanically with a Wig-I-bug shaking machine.

So that the material would closely resemble the natural samples, the sulphides of the volatile elements were incorporated into the matrix by a vacuum-fusion technique at 800 °C. The product was then cooled, ground, and mixed in the manner already described. Details of the procedure are given in the Appendix.

### 2.2. PREPARATION OF CALIBRATION STANDARDS

A set of five calibration standards was prepared from the trace-element mixtures and the synthetic matrix material, which were mixed in the proportions given in Table I-3 of the Appendix. The constituents were mixed thoroughly by being ground in an agate mortar under acetone, and dried at 80 °C. The mixture was transferred to a 13 mm by 5 mm plastic vial containing a Plexiglass ball and was shaken on the mixer mill for 5 minutes.

### 2.3. BUFFER

Previous work had shown that lithium fluoride (in a ratio to graphite of 1 to 4) was an effective buffer for use in the analysis of trace elements<sup>4</sup>. Lithium fluoride was therefore added to all the samples and standards before they were excited for the analysis. It was mixed with the sample in a ratio of 2 parts of buffer mixture to 1 part of sample.

### 2.4. INTERNAL STANDARDS

The choice of a satisfactory internal standard was complicated by the fact that the material to be analysed contained a large number of elements of analytical interest and of varying volatilities. Several elements, including scandium, germanium, palladium, and gold, were tested as possible internal standards. Germanium had been used with success in a method for the analysis of geological samples for trace elements<sup>4</sup>, but it was found that the sulphide samples had sometimes to be analysed for germanium, which can be present in small and variable amounts. Scandium gave satisfactory results only for the refractory elements.

Tests with palladium and gold as internal standards for the volatile elements indicated that only gold was satisfactory. Therefore, a combination was adopted: scandium for the refractory elements (chromium, titanium, calcium, molybdenum, vanadium, zirconium, and aluminium) and gold for the more volatile elements (cadmium, cobalt, beryllium, magnesium, arsenic, antimony, bismuth, nickel, germanium, tin, silver, and boron).

The concentrations of the internal-standard compounds in the buffer mixture were scandium oxide ( $\text{Sc}_2\text{O}_3$  0.05 per cent) and gold (0.02 per cent). The gold was added as the ammonium chloroaurate complex, its exact gold content having been established after its reduction to the metal with hydrogen<sup>5</sup>.

### 2.5. CONDITIONS FOR EXCITATION

The equipment used for the excitation of the samples and recording of the spectra is listed in Section 3 of the Appendix. During the initial attempts to excite the sample-buffer mixtures, the invert-packing technique into necked electrodes (Ringsdorff RW 0041) was used. It was found that the sample was very often ejected immediately after initiation of the arc, apparently as a result of the sudden evolution of gases in the charge. The problem was solved by heating of the loaded electrodes in an oven at 110 °C for two hours, followed by the use of a 'split-burn' technique, during which the sample is first excited at a current of 4 A for 10 seconds, and finally at 12 A for 80 seconds for copper and lead concentrates and for 70 seconds for the zinc concentrates. A significant improvement in the stability of the arc and resulting reproducibility of the results was observed when a modified 'double-flow' Stallwood jet<sup>6</sup>, with an atmosphere consisting of 80 per cent argon and 20 per cent oxygen with a sheathing flow of pure argon, was used to stabilize the discharge.

## 3. ACCURACY AND PRECISION

As indicated in Section 1, calibration standards were prepared on the basis of an average matrix composition for a large number of samples. This average was derived from data obtained by atomic-absorption spectroscopy and by an X-ray unit having an isotopic source. No systematic examination of matrix effect was undertaken because of the time involved, but some indications of the relative absence of matrix effects are given by the general agreement between the present values and those obtained by atomic-absorption spectrophotometry (AAS)<sup>7</sup>, instrumental neutron-activation analysis (INAA)<sup>8</sup>, liquid-liquid extraction<sup>9</sup>, and chemical procedures<sup>10</sup> (see Table 4).

## SPECTROGRAPHIC ANALYSIS OF CONCENTRATES

The precision of the method (see Table 5) was established by analysis of the three concentrates twelve times on several plates over a period of time, and represents the level of precision that can be expected in normal routine analysis. This precision can be regarded as very satisfactory for a rapid photographic technique.

It can be noted that the sensitivity obtainable for zinc concentrates is much higher than that for copper and lead concentrates because of its high volatility and excitation potential.

### 4. MATRIX VARIATIONS

A comparison of the composition of the samples analysed (see Table 4) and that for the average matrix compositions for typical copper, lead, and zinc concentrates (see Table 6) suggests that the procedures, particularly for lead and zinc concentrates, have some tolerance to matrix variations. For assessment of what kind of matrix variation could be tolerated, tests were conducted with mixtures of the samples listed in Table 4.

The analyses of these mixtures were compared with values calculated from the results reported on the original samples so that the consistency of the spectrographic data could be shown, and also with the average values calculated from those obtained by different procedures so that the accuracy could be assessed (see Table 7).

The matrix variations, i.e., the agreement between the determined values and those calculated from the original analysis (both spectrographically and by other methods), of the individual concentrates are generally within 15 per cent, i.e., to within twice the average standard deviation of all the elements determined spectrographically. The exceptions are magnesium and molybdenum in copper and lead concentrates, and cobalt in zinc concentrates.

### 5. DISCUSSION

In general, where comparisons are possible, the agreement is satisfactory in view of the fact that similar errors of determination can be attributed to each of the procedures involved. No values are quoted for cadmium and aluminium. The overall accuracy and precision for cadmium is limited by the low contrast factor for the plate emulsion at low wavelength, and by self absorption at high concentrations. For aluminium, no lines that were completely free from interference could be found within the range of wavelengths covered, i.e., 230 to 350 nm.

The determination of silver is limited by the high sensitivity of the only lines available for measurement. The limits of detection are relatively high for the volatile elements, which are volatilized rapidly in the early stages of excitation and which generally have high ionization potentials.

Since the results given in Table 7 indicate that a reasonable range of matrix variation can be tolerated, it should be possible for matrix variations in samples to be limited by the addition of synthetic matrix sulphide to give a matrix composition resembling that of the calibration standards. However, the sensitivity will be reduced, contamination may occur, and additional time is involved in the preparation of the matrix addition and its blending with the sample.

Despite its limitations, the procedure is capable of giving information on a greater number of elements than is any other method examined. One of the major reasons for the improved accuracy of the proposed technique is the preparation, for the calibration standards, of matrix materials that are similar in composition and form to those of the samples to be analysed.

Although the precision obtained is very good for a photographic technique, it is reasonable to assume that an improvement in the precision and the time taken for analysis could be effected by the use of a direct-reading spectrometer, although the use of two internal standards would raise problems that would have to be resolved.

Currently, the time required for the analysis of a batch of six samples for 20 elements is 12 hours, provided that calibration standards are available.

### 6. CONCLUSIONS

The proposed procedure provides a rapid and convenient method for the analysis of sulphide concentrates for minor and trace elements. There is a minimum of sample preparation, and, for many of the elements, the concentration ranges covered are satisfactory for analyses to be used for the determination of the specifications of the materials. The accuracy of the method is about 10 per cent, and the precision varies for the different elements from 2 to 13 per cent. The procedure is essentially applicable to true concentrates. For the analysis of beneficiation products that may have widely

## SPECTROGRAPHIC ANALYSIS OF CONCENTRATES

differing compositions, some attempt could be made to match the average matrix composition of the calibration standards more closely by dilution with copper, lead, zinc, or iron sulphides. However, a significant loss of sensitivity will occur.

### 7. REFERENCES

1. ERDEY, L. International series of monographs on analytical chemistry. London, Pergamon Press, 1965. *Gravimetric analysis*, part II, vol. 7.
2. HANSEN, M. Constitution of binary alloys. New York, McGraw-Hill Book Co. Inc., 1958.
3. MAYS, R.E., CZAMANSKE, G.K., and HERAPOULAS, C. Synthetic standards for quantitative emission spectrographic analysis. *Appl. Spectrosc.*, vol. 28, no. 5. 1974. pp. 462-467.
4. WATSON, A.E., RUSSELL, G.M., and STEELE, T.W. The analysis of geological samples for trace elements by direct-reading emission spectrometry. Johannesburg, National Institute for Metallurgy, *Report no. 1656*. Sep. 1974.
5. SCHOELLER, W.R., and POWELL, A.R. Analysis of minerals and ores of the rarer elements. London, C. Griffin and Co., Nov. 1955. p. 352.
6. BAUMANS, P.W.J.M., and MAESSEN, F.J.M.N. *Spectrochim. Acta*, vol. 24B. 1969. pp. 585-610.
7. ROBERT, R.V.D., MALLETT, R.C., and STEELE, T.W. Laboratory Method no. 13/10. The determination, by atomic-absorption spectrophotometry, of minor elements in zinc, lead, and copper sulphide concentrates. Johannesburg, National Institute for Metallurgy, *Report no. 1746*. 11th Jul., 1975.
8. PEARTON, D.C.G., EDDY, B.T., BIBBY, D.M., STEELE, T.W., and SELLSCHOP, J.P.F. The determination, by instrumental neutron-activation analysis, of some trace elements in sulphide ores and concentrates. Johannesburg, National Institute for Metallurgy, *Report no. 1792*. (To be published.)
9. NICOLAS, D.J., and STEELE, T.W. The application of three-phase liquid-liquid extraction to the analysis of bismuth and tellurium in sulphide concentrates. Johannesburg, National Institute for Metallurgy, *Report no. 1794*. (To be published.)
10. JONES, E.A., and STEELE, T.W. The determination, by atomic-absorption spectrophotometry, of trace elements in sulphide concentrates. Johannesburg, National Institute for Metallurgy, *Report no. 1787*. (To be published.)



SPECTROGRAPHIC ANALYSIS OF CONCENTRATES

TABLE 1

*Composition of the samples*

Type of concentrate	Amount present, %		
	Copper	Lead	Zinc
Copper	20 to 30	1 to 10	1 to 10
Lead	1 to 5	20 to 70	1 to 15
Zinc	0,5 to 2	1 to 20	30 to 35

TABLE 2

*Composition of the copper, lead, and zinc matrices*

Material added	Concentrates		
	Copper	Lead	Zinc
CuS, %	33,0	3,0	0,75
PbS, %	9,2	69,0	1,15
ZnS, %	7,1	4,9	73,10
Fe S <sub>2</sub> , %	32,1	21,4	21,4
Fe <sub>2</sub> O <sub>3</sub> , %	14,3	—	—
SiO <sub>2</sub> , %	4,3	1,7	3,6

SPECTROGRAPHIC ANALYSIS OF CONCENTRATES

TABLE 3  
Composition of the trace-element mixtures

element	Mixture A		Mixture B		Mixture C*		Mixture D		Mixture E	
	Mass mg	Metal in the composite %	Metal in the composite†	Mass mg	Metal in the composite†	Mass mg	Metal in the composite†	Mass mg	Metal in the composite†	Mass mg
MgO	166	10	ZrO <sub>2</sub>	54.0	Sb <sub>2</sub> S <sub>3</sub>	55.7	ZrO <sub>2</sub>	Mixture of equal parts of B and C	ZrO <sub>2</sub>	Mixture of D and matrix 120/680
Mn <sub>3</sub> O <sub>4</sub>	139	10	NiO	50.8	CdS	51.3	NiO		NiO	
Al <sub>2</sub> O <sub>3</sub>	189	10	V <sub>2</sub> O <sub>5</sub>	71.6	Bi <sub>2</sub> S <sub>3</sub>	49.4	V <sub>2</sub> O <sub>5</sub>		V <sub>2</sub> O <sub>5</sub>	
CaCO <sub>3</sub>	75	3	BeO	110.8	As <sub>2</sub> S <sub>3</sub>	65.7	BeO		BeO	
Cr <sub>2</sub> O <sub>3</sub>	43.8	3	H <sub>3</sub> BO <sub>3</sub>	228.4	SnS <sub>2</sub>	61.6	H <sub>3</sub> BO <sub>3</sub>		H <sub>3</sub> BO <sub>3</sub>	
Co <sub>3</sub> O <sub>4</sub>	40.8	3	MoO <sub>3</sub>	60.0			MoO <sub>3</sub>		MoO <sub>3</sub>	
TiO <sub>2</sub>	48.2	3	GeO <sub>2</sub>	57.6			GeO <sub>2</sub>		GeO <sub>2</sub>	
AgCl	40	3					Sb <sub>2</sub> S <sub>3</sub>		Sb <sub>2</sub> S <sub>3</sub>	
							CdS		CdS	
							Bi <sub>2</sub> S <sub>3</sub>		Bi <sub>2</sub> S <sub>3</sub>	
Matrix‡	258.2	—	Matrix	366.8	Matrix	716.3	As <sub>2</sub> S <sub>3</sub>	As <sub>2</sub> S <sub>3</sub>		
							SnS <sub>2</sub>	SnS <sub>2</sub>		

\* Material to be sintered before being used for the preparation of mixture D.

† Each metal represents 4 per cent of the composite in mixtures B and C, and 2 per cent and 0.3 per cent of the composite in mixtures D and E respectively.

‡ See Table 2.

SPECTROGRAPHIC ANALYSIS OF CONCENTRATES

TABLE 4  
Values obtained by various techniques for sulphide materials

Elements	Cu concentrates 33/74				Pb concentrates 32/74				Zn concentrates 31/74			
	Spectro- graphic analysis	AAS without separation	AAS with separation*	INAA	Spectro- graphic analysis	AAS without separation	AAS with separation*	INAA	Spectro- graphic analysis	AAS without separation	AAS with separation*	INAA
Mn, %	1,00	1,22	1,10	1,20	1,00	1,13	0,43	1,10	1	3,25	1,15	3,30
Ca, p.p.m.	1 080	1 185	-	-	865	933	-	-	> 3 000	11 000	-	-
Cr, p.p.m.	1 280	1 388	1 600	1 330	1 940	3 200	3 085	2 800	<	< 200	< 20	< 100
Bi, p.p.m.	377	341	318	-	> 300	1 393	1 156	124	54	62	83	-
Co, p.p.m.	178	215	-	208	153	149	-	-	1 140	1 035	-	933
Mg, p.p.m.	647	650	-	-	658	652	-	-	1 694	1 990	-	-
Cd, p.p.m.	u	144	-	194	u	883	-	105	1 694	1 068	-	960
Ni, p.p.m.	27	-	-	< 500	12	-	-	< 500	26	< 200	-	-
Mo, p.p.m.	33	-	-	71	43	-	-	45	3	-	-	-
V, p.p.m.	< 10	-	< 50	< 10	15	-	< 50	< 10	3	-	< 50	< 5
Ti, p.p.m.	<	-	-	-	51	-	-	-	103	-	-	-
Bc, p.p.m.	<	-	-	-	< 3	-	-	-	3,7	-	-	-
Sb, p.p.m.	< 100	77	65	73	290	271	-	220	<	29	31	15
As, p.p.m.	< 100	-	-	-	< 100	3,8	< 50	-	<	3,7	< 50	-
Zr, p.p.m.	< 100	-	-	-	< 10	-	< 50	-	10	-	<	-
Sn, p.p.m.	< 30	-	< 50	-	< 10	-	< 50	-	<	-	<	-
Ce, p.p.m.	< 10	-	-	-	< 10	-	-	-	<	-	<	-
Al, p.p.m.	Δ	< 1 000	520	260	Δ	< 1 000	623	530	Δ	3 100	3 100	2 100
Ag, p.p.m.	> 30	575	-	650	> 30	771	-	774	>	38	-	53

\* Separation by coprecipitation with lanthanum hydroxide.

u = Results obtained are unreliable.

Δ = Spectral lines too strong or too weak, or showed interference from other elements.

**SPECTROGRAPHIC ANALYSIS OF CONCENTRATES**

**TABLE 5**

*Precision of the method*

Element	Cu concentrates 33/74		Pb concentrates 32/74		Zn concentrates 31/74	
	Av. result p.p.m.	Coefficient of variation %	Av. result p.p.m.	Coefficient of variation %	Av. result p.p.m.	Coefficient of variation %
Co	182	5,8	191	4,3	1 096	2,6
Mn	0,94*	6,4	0,99*	5,6	—	—
Cr	1 175	6,1	1 611	4,0	—	—
Mg	736	6,0	693	3,9	1 883	8,5
Ni	24	12,6	9,9	8,6	26	4,2
Mo	—	—	30	10,4	—	—
Bi	336	6,8	—	—	53	9,7
Ti	58	11,8	6	10,3	91	5,8
Ca	980	5,0	1 014	5,3	—	—

\* Per cent

**TABLE 6**

*Composition of the matrices of the samples and standards analysed*

Element	Cu concentrates, %			Pb concentrates, %			Zn concentrates, %			Standard
	Sample no.		Standard	Sample no.		Standard	Sample no.			
	1 (33/74)	2*		1 (32/74)	2†		1 (31/74)	2‡	3§	
Cu	21	15,6	22	1	11	2	0,4	7,3	10,7	0,5
Pb	17	13,3	8	75	46	60	2	7,0	9,5	1
Zn	7	16,5	5	3	5	3	45	32,3	26	49
Fe	21	18,0	27	3	12	10	9	13	15	10
S	28	28,3	30	14	21	23	29	28,7	28,5	36

\* Cu concentrate no.2 = 3 parts of 33/74 + 1 part of 31/74

† Pb concentrate no.2 = 1 part of 32/74 + 1 part of 33/74

‡ Zn concentrate no.2 = 2 parts of 31/74 + 1 part of 33/74

§ Zn concentrate no. 3 = 1 part of 31/74 + 1 part of 33/74

TABLE 7

Comparison of results obtained on mixed concentrates  
with calculated values

Element	Cu concentrate no. 2*			Pb concentrate no. 2*			Zn concentrate no. 2*			Zn concentrate no. 3*		
	Results, p.p.m.†			Results, p.p.m.†			Results, p.p.m.†			Results, p.p.m.†		
	Actual	Calc. spec.‡	Mean ¶	Actual	Calc. spec.‡	Mean ¶	Actual	Calc. spec.‡	Mean ¶	Actual	Calc. spec.‡	Mean ¶
Co	408	418	390	159	166	172	844	819	730	748	659	598
Mg	758	909	960	463	653	648	1 580	1 345	1 486	1 390	1 170	1 276
Cr	992	960	992	1 980	1 630	2 084	441	430	449	616	640	665
Ni	24	27	28	24	20	24	30	26	27	30	27	26
Bi	266	297	309	> 300	> 300	784	185	162	163	215	215	211
Ti	81	71	78	63	56	68	88	89	90	80	81	85
Ce	> 3 000	> 3 000	4 707	923	972	989	> 3 000	> 3 000	7 625	> 3 000	> 3 000	5 987
Mo	17	25	40 to 43	75	43	50	29	11	19 to 26	36	17	28 to 33
Mn	1,48%	1,55%	1,62%	0,94%	1,00%	1,08%	1,00%	1,00%	2,44%	> 1,00%	> 1,00%	211
Sb	< 100	< 100	59	161	145	166	< 100	< 100	40	< 100	< 100	48
V	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10

\* See Table 6.

† Except where indicated as per cent

‡ Mean calculated results obtained from the spectrographic determination of concentrates 31/74, 32/74, and 33/74

¶ Mean calculated results obtained from all available results given by various techniques (see Table 4)

## APPENDIX

**THE SPECTROGRAPHIC DETERMINATION OF MINOR AND TRACE  
ELEMENTS IN COPPER, LEAD, AND ZINC CONCENTRATES  
(LABORATORY METHOD NO. 16/20)**

**1. OUTLINE OF METHOD**

The sample is mixed with an internal standard—buffer mixture in the ratio of 1 part of sample to 2 parts of mixture. The internal standard—buffer mixture consists of 4 parts of  $Sc_2O_3$  (0,05 per cent) and gold (0,02 per cent) in graphite to 1 part of lithium fluoride. The electrodes are packed by use of the invert-packing technique, tamped, and pierced. Spectrograms are taken of the composite mixture, and comparisons are made with those obtained from synthetically prepared standards.

**2. APPLICATION OF METHOD**

The method is applicable to the determination of twenty trace and minor impurities in copper, lead, and zinc sulphide concentrates. The overall precision was found to be between 4 and 12 per cent.

**3. APPARATUS**

- (1) *Spectrograph*  
Jarrell-Ash 3,4 metre Ebert (1200 lines per millimetre of grating)
- (2) *Excitation Source*  
Jarrell-Ash Custom Varisource
- (3) *Microphotometer*  
Hilger and Watts console with digital read out
- (4) *Stallwood Jet*  
Baumans and Maessen design<sup>1</sup>
- (5) *Photoprocessor*  
Jarrell-Ash Photoprocessor
- (6) *Plates*  
Agfa-Gevaert Scientia Plates, type 34B 50  
(2 plates in the middle of the camera)
- (7) *Electrodes*  
Ringsdorff R.W. 0041 undercut (bottom electrode)
- (8) *Calculator*  
Respectra Spectrochemical Calculator.

**4. REAGENTS**

- (1) *Graphite*  
Ringsdorff grade R.W.A.
- (2) *Lithium Fluoride*  
Spex Industries (5 to 9 S)
- (3) *Scandium Oxide*  
Johnson Matthey Specpure
- (4) *Ammonium Chloroaurate*  
Johnson Matthey Specpure
- (5) *Adefo Rapid X-ray Developer*
- (6) *Amfix High-speed Fixer*  
May and Baker
- (7) *Hardener Type S*  
May and Baker.

**5. PREPARATION OF THE INTERNAL STANDARD—BUFFER MIXTURE****5.1. GOLD (0,1 PER CENT) IN GRAPHITE**

- a. Prepare a mixture of gold (10 per cent) in graphite as follows. Determine the gold content of the

## SPECTROGRAPHIC ANALYSIS OF CONCENTRATES

ammonium chloroaurate by reduction under hydrogen<sup>2</sup>, and transfer the equivalent of 50 mg of gold to an agate mortar. Add graphite to make up to 500 mg and mix under acetone. Dry in an oven at 100 °C, and store in a plastic vial.

- b. Dilute 50 mg of this mixture with 450 mg of graphite by grinding in a mortar under acetone to give a mixture of 1 per cent gold in graphite.
- c. Dilute 50 mg of the mixture of 1 per cent gold and graphite with 450 mg of graphite as before, to give a mixture of 0,1 per cent gold in graphite. Store in a plastic vial.

### 5.2. SCANDIUM OXIDE (0,1 PER CENT) IN GRAPHITE

- a. Prepare a mixture of Sc<sub>2</sub>O<sub>3</sub> (10 per cent) in graphite by grinding 50 mg of scandium oxide with 450 mg of graphite under acetone in an agate mortar. Dry in an oven at 100 °C and then store in a plastic vial.
- b. Dilute 50 mg of this mixture with 450 mg of graphite by grinding in an agate mortar under acetone as before, to give a mixture of Sc<sub>2</sub>O<sub>3</sub> (1 per cent) in graphite.
- c. Dilute 50 mg of the mixture with 450 mg of graphite as before, to give a graphite mixture having the required scandium oxide content of 0,1 per cent. Store in a plastic vial.

### 5.3. INTERNAL STANDARD-BUFFER MIXTURE

The mixture consists of 4 parts of internal standard, i.e., Sc<sub>2</sub>O<sub>3</sub> (0,05 per cent) and gold (0,02 per cent) in graphite, to 1 part of lithium fluoride.

- a. Crush 450 mg of lithium fluoride in an agate mortar.
- b. Add 900 mg of Sc<sub>2</sub>O<sub>3</sub> (0,1 per cent) in graphite, 360 mg of gold (0,1 per cent) in graphite, and 540 mg of graphite, and mix well under acetone.
- c. Dry in an oven at 100 °C and store in a plastic vial.

## 6. EXPERIMENTAL CONDITIONS

The experimental conditions are given in Table I-1.

## 7. STANDARDS

### 7.1. PREPARATION OF THE COPPER, LEAD, AND ZINC MATRIX

- a. Prepare copper, lead, zinc, and iron sulphides from Specpure metals by the method described by Erdy<sup>3</sup> and Hansen<sup>4</sup>.
- b. Transfer the weighed sulphides (see Table I-2) to an agate mortar, add acetone to form a slurry, and grind well to give a homogeneous mixture.
- c. Dry in an oven at 80 °C, transfer to a plastic vial with 3 Plexiglass balls, and shake mechanically with a Wig-l-bug shaking machine for 15 minutes.

### 7.2. PREPARATION OF BASIC TRACE-ELEMENT MIXTURES

- a. Prepare the trace-element mixtures (given in Table I-3) by weighing out appropriate amounts of oxides and sulphides, and grinding them together in an agate mortar under acetone.
- b. Dry in an oven at 80 °C, transfer to plastic vials, and blend further mechanically with a Wig-l-bug shaking machine for 10 minutes.
- c. To prepare mixture C, divide the combined and mixed sulphides into three portions and transfer them to three quartz tubes (see Figure I-1).
- d. Evacuate the tubes under 37,5 cm of mercury for 30 minutes, and seal under vacuum using an oxyacetylene torch.
- e. Place the tubes into mild-steel jackets plugged at one end with asbestos string (see Note 1).
- f. Place the tubes in a muffle furnace and gradually raise the temperature to 800 °C in steps of 100 °C for every 30 minutes.
- g. Hold the temperature for 2 hours at 800 °C and then lower the temperature to 400 °C over a period of 2 hours.
- h. Switch off the muffle furnace and allow it to cool overnight.
- i. Remove and transfer the sintered standard to an agate mortar, and grind to a fine powder under acetone.
- j. Dry in an oven at 80 °C, transfer to a plastic vial, and blend further with a Wig-l-bug shaking machine for 10 minutes.

### 7.3. PREPARATION OF CALIBRATION STANDARDS

The calibration standards to be used are given in Table I-4.

Prepare five standards by combining the materials given in Table I-5 and mixing thoroughly, as described in Section 7.2.

## SPECTROGRAPHIC ANALYSIS OF CONCENTRATES

### 8. PROCEDURE

#### 8.1. PREPARATION OF SAMPLES AND PACKING OF ELECTRODES

- a. Mix 80 mg of the sample with 150 mg of the internal standard-buffer mixture in a plastic vial with a Plexiglass ball on a mixer mill for 6 minutes.
- b. Remove the Plexiglass ball from the vial and press the electrode into the mixed sample until the cavity is full.
- c. Tamp and pierce the packed sample with the special tool provided.
- d. Dry in an oven at 100°C for 2 hours. Treat all the standards and samples similarly.

#### 8.2. EXCITATION OF SAMPLE AND PROCESSING OF RECORDED SPECTRA

- a. Expose a reference spectrum for iron for 6 seconds at 4 A, and expose the standards and samples under the conditions given in Table I-1.
- b. Process the exposed plates as described in Table I-1, and dry them in a stream of hot air.
- c. Read, on the microphotometer, the percentage transmittance of suitable iron lines in both exposure steps of the reference spectrum for iron, and construct an emulsion-calibration curve on the calculation board using the *K* and *Y* values calculated according to the two-step method of Honerjäger-Sohm and Kaiser<sup>5</sup>.
- d. Read the percentage transmittance of appropriate analytical and internal-standard lines in Table I-6 for the various elements in the standards and samples, and convert the values to log-intensity ratios from the emulsion-calibration curve.
- e. Construct calibration curves on semilogarithmic graph paper for the various elements, plotting log-intensity ratios against concentration of the standards, and derive the concentration of these elements in the samples from their respective curves.

### 9. NOTES

- (1) This precautionary measure is taken because faulty tubes may fracture under pressure at elevated temperatures.

### 10. REFERENCES

1. BOUMANS, P.W.J.M., and MAESSEN, F.J.M.N. *Spectrochim. Acta*, vol. 24B, 1969, pp. 585-610.
2. SCHOELLER, W.R., and POWELL, A.R. Analysis of minerals and ores of the rarer elements. London, C. Griffin and Co., Nov. 1955, pp. 352.
3. ERDEY, L. International series of monographs on analytical chemistry, vol. 7. Gravimetric analysis, Part II. London, Pergamon Press, 1965.
4. HANSEN, M. Constitution of binary alloys. New York, McGraw-Hill Book Co. Inc., 1958.
5. HONERJÄGER-SOHN, M., and KAISER, H. *Spectrochim. Acta*, vol. 2, no. 8, 1944, pp. 396-416.



SPECTROGRAPHIC ANALYSIS OF CONCENTRATES

TABLE I-1

*Conditions for the excitation of copper, lead, and zinc concentrates*

Grating angle	10,00 (225,0 nm to 350,0 nm)
Slit width	20 $\mu$ m
Slit height	2 mm
Filter	4th filter (transmission 26,7 per cent)
Analytical gap	4 mm
Excitation and exposure	
(a)	4 A direct current for 10 s, instantly switching to
(b)	12 A direct current (80 s for copper and lead concentrates and 70 s for zinc concentrate)
Controlled atmosphere	Argon 80 % (Rotameter 25), oxygen 20 % (Rotameter 4), tangential argon 4 l/min
Photo-processing	Develop for 5 min in Adefo X-ray Developer 15 s in stopbath (1 per cent acetic acid soln) 3½ min in Amfix High Speed Fixer Wash for 10 min in running water Dry for 10 min in a stream of warm air

TABLE I-2

*Composition of the copper, lead, and zinc matrix*

Metals added	Cu conc. g	Pb conc. g	Zn conc. g
CuS	3,30	0,30	0,075
PbS	0,92	6,90	0,115
ZnS	0,71	0,49	7,310
FeS <sub>2</sub>	3,21	2,14	2,140
Fe <sub>2</sub> O <sub>3</sub>	1,43	—	—
SiO <sub>2</sub>	0,43	0,17	0,360

TABLE 1-3

## Composition of trace-element mixtures

Mixture A			Mixture B		Mixture C*		Mixture D		Mixture E	
Element	Mass mg	Metal in the composite %	Metal in the composite†	Mass mg	Metal in the composite†	Mass mg	Metal in the composite†	Mass mg	Metal in the composite†	Mass mg
MgO	166	10	ZrO <sub>2</sub>	54,0	Sb <sub>2</sub> S <sub>3</sub>	55,7	ZrO <sub>2</sub>	Mixture of equal parts of B and C	ZrO <sub>2</sub>	Mixture of 120/680
Mn <sub>3</sub> O <sub>4</sub>	139	10	NiO	50,8	CdS	51,3	NiO		NiO	
Al <sub>2</sub> O <sub>3</sub>	189	10	V <sub>2</sub> O <sub>5</sub>	71,6	Bi <sub>2</sub> S <sub>3</sub>	49,4	V <sub>2</sub> O <sub>5</sub>		V <sub>2</sub> O <sub>5</sub>	
CaCO <sub>3</sub>	75	3	BeO	110,8	As <sub>2</sub> S <sub>3</sub>	65,7	BeO		BeO	
Cr <sub>2</sub> O <sub>3</sub>	43,8	3	H <sub>3</sub> BO <sub>3</sub>	228,4	SnS <sub>2</sub>	61,6	H <sub>3</sub> BO <sub>3</sub>		H <sub>3</sub> BO <sub>3</sub>	
Co <sub>3</sub> O <sub>4</sub>	40,8	3	MoO <sub>3</sub>	60,0			MoO <sub>3</sub>		MoO <sub>3</sub>	
TiO <sub>2</sub>	48,2	3	GeO <sub>2</sub>	57,6			GeO <sub>2</sub>		GeO <sub>2</sub>	
AgCl	40	3					Sb <sub>2</sub> S <sub>3</sub>		Sb <sub>2</sub> S <sub>3</sub>	
							CdS		CdS	
Matrix‡	258,2	—	Matrix	366,8	Matrix	716,3	Bi <sub>2</sub> S <sub>3</sub>		Bi <sub>2</sub> S <sub>3</sub>	
							As <sub>2</sub> S <sub>3</sub>	As <sub>2</sub> S <sub>3</sub>		
							SnS <sub>2</sub>	SnS <sub>2</sub>		

\* Material to be sintered before being used for the preparation of mixture D.

† Each metal represents 4 per cent of the composite in mixtures B and C, and 2 per cent and 0,3 per cent of the composite in mixtures D and E respectively.

‡ See Table 1-2.

**SPECTROGRAPHIC ANALYSIS OF CONCENTRATES**

**TABLE I-4**

*Calibration standards to be used*

Elements to be determined	Standards				
	No. 1	No. 2	No. 3	No. 4	No. 5
Mg, Mn, Al, %	1	0,3	0,1	0,03	0,01
Ag, Ca, Cr, Co, Ti, p.p.m.	3000	1000	300	100	30
Sb, Cd, Mo, Zr, Ni, Bi, V, As, Be, B, Sn, Ge, p.p.m.	300	100	30	10	3

**TABLE I-5**

*Composition of calibration standards*

Standard no.	Mixture	Amount, mg
1	A	150
	E	150
	Matrix*	1200
2	Standard no. 1	333,3
	Matrix	666,7
3	Standard no. 1	100
	Matrix	900
4	Standard no. 2	100
	Matrix	900
5	Standard no. 3	100
	Matrix	900

\* See Table I-2

TABLE 1-6  
Analytical lines

Analytical lines					Analytical lines				
Element considered			Internal standard		Element considered			Internal standard	
Element	Length nm	Range of concentration p.p.m.	Element	Length nm	Element	Length nm	Range of concentration p.p.m.	Element	Length nm
Cd (1)	228,8	300 to 3	Au (1)	242,8	Mg (1)*	278,1	10 <sup>4</sup> to <100	Au (1)	242,8
Be (1)	234,9	300 to <3	Au (1)	242,8	Cr (11)	284,3	3000 to 30	Sc (11)	336,2
As (1)	235,0	300 to <100	Au (1)	242,8	Ni (1)	305,1	300 to <10	Au (1)	312,3
Co (1)*	242,5	3000 to <30	Au (1)	242,8	Bi (1)	306,8	300 to <30	Au (1)	312,3
Sn (1)	242,9	300 to 30	Au (1)	242,8	Ca (11)*	315,9	3000 to <30	Sc (11)	336,2
B (1)	249,8	300 to 10	Au (1)	242,8	Mo (1)	317,0	300 to <10	Sc (11)	336,2
Mn (1)*	258,4	10 <sup>4</sup> to <100	Sc (11)	255,2	V (1)	318,3	300 to <3	Sc (11)	336,2
Sb (1)	259,8	300 to 100	Au (1)	242,8	Zr (11)	339,2	300 to 30	Sc (11)	336,2
Ge (1)	265,1	300 to <10	Au (1)	242,8	Ti (1)	337,1	3000 to <30	Sc (11)	336,2
Al (1)†	265,2	10 <sup>4</sup> to <100	Sc (11)	255,2	Ag (1)‡	338,3	< 30	Au (1)	312,3

\* Line selected to cover the required concentration range.

† Only usable line at this concentration and has an interference from manganese.

‡ Silver lines in wavelength region very sensitive.

SPECTROGRAPHIC ANALYSIS OF CONCENTRATES

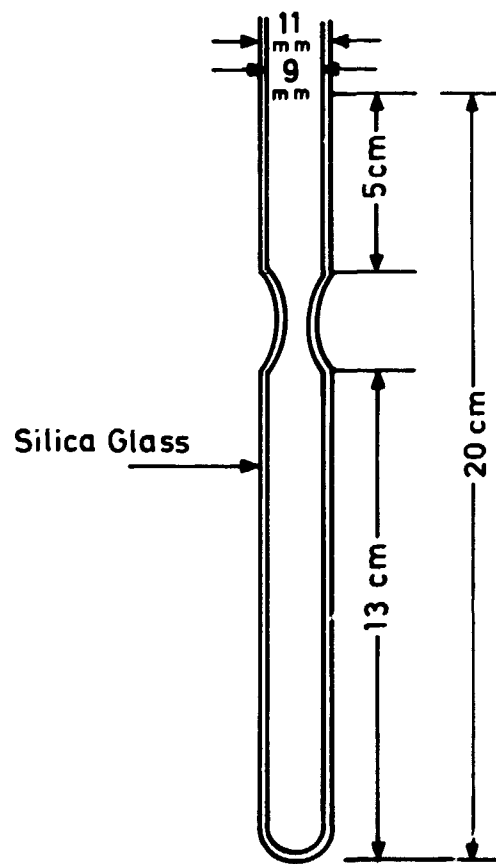


FIGURE I-1 Silica-glass tubes for sintering of volatile elements