

2

**REPORT**

No. 1794

**THE APPLICATION OF THREE-PHASE  
LIQUID-LIQUID EXTRACTION TO THE  
ANALYSIS OF BISMUTH AND TELLURIUM  
IN SULPHIDE CONCENTRATES**

**Director of Division** T.W. Steele

**Investigator** D.J. Nicolas

**Date** 27th February, 1976

**Project** 08274

**Project Report No.** 1

**NATIONAL  
INSTITUTE  
for  
METALLURGY**

1 Yale Road,  
Milner Park,  
JOHANNESBURG,  
South Africa.



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

**REPORT ● VERSLAG**

**No. 1794**

**THE APPLICATION OF THREE-PHASE LIQUID-LIQUID EXTRACTION TO  
THE ANALYSIS OF BISMUTH AND TELLURIUM IN SULPHIDE CONCENTRATES**

**27th February, 1976**

**Investigator: D.J. Nicolas**

**ISBN 0 86999 257 0**

## SYNOPSIS

An extraction system consisting of one aqueous and two organic phases is described. Dianripyrylmethane (DAM) is used as the extractant for bismuth and tellurium, which are extracted into the smaller of the two organic phases from nitric acid and perchloric acid respectively.

The extraction efficiency is in the range of 90 to 95 per cent, compensation for incomplete extraction being made by the technique of standard addition. Copper, lead, and zinc are not extracted in either procedure. When the solutions contain high concentrations of iron, thioglycolic acid is used as a masking agent for iron in the extraction of bismuth.

Atomic-absorption spectrophotometry is used for the analysis of the third phase after it has been diluted with methanol. The precision for bismuth and tellurium is in the range of 3 to 4 per cent. The accuracy, as ascertained from comparative analyses of sulphide concentrates, is good.

## SAMEVATTING

'n Ekstraksiestelsel bestaande uit een waterige en twee organiese fases word beskryf. Dianripyrylmetaan (DAM) word gebruik as ekstraheermiddel vir bismut en telluur wat onderskeidelik uit salpetersuur en perchloorsuur in die kleinste van die twee organiese fases in geëkstraheer word.

Die ekstraksierendement is in die omgewing van 90 tot 95 persent en daar word vir die onvolledige ekstraksie gekompenseer deur die tegniek van standaardbyvoeging. Koper, lood en sink word nie in een van die prosedures geëkstraheer nie. As die oplossings hoë ysterkonsentrasies bevat, word tioglikolsuur by die ekstraksie van bismut as 'n maskeermiddel vir yster gebruik.

Atoomabsorpsiespektrofotometrie word gebruik vir die ontleding van die derde fase nadat dit met metanol verdun is. Die presisie vir bismut en telluur is in die omgewing van 3 tot 4 persent. Die akkuraatheid soos aan die hand van vergelykende ontledings van sulfiedkonsentrate bepaal, is goed.

## CONTENTS

1.	INTRODUCTION	1
2.	EXPERIMENTAL METHOD	1
	2.1. EXTRACTION OF BISMUTH AND TELLURIUM	1
	2.1.1. Effect of Acidity	1
	2.1.2. Equilibration Time	2
	2.1.3. Effect of Varying Phase Ratios	3
	2.1.4. Effect of Diluent Composition on Extraction	3
	2.2. CO-EXTRACTION OF MATRIX ELEMENTS	3
	2.3. ELIMINATION OF INTERFERENCES IN THE DETERMINATION OF BISMUTH	4
3.	PROCEDURE	6
4.	APPLICATION TO THE ANALYSIS OF SULPHIDE CONCENTRATES	6
5.	DISCUSSION	6
6.	CONCLUSION	6
7.	REFERENCES	8
Table 1	Extraction of the tellurium-bromide complex from a perchloric acid medium	2
Table 2	Third-phase formation in the presence of perchloric acid	3
Table 3	Co-extraction of matrix elements and extraction of bismuth in their presence	4
Table 4	Co-extraction of matrix elements and extraction of tellurium in their presence	5
Table 5	Effect of thioglycolic acid on the extraction of bismuth	5
Table 6	Comparative analyses of sulphide concentrates	7
APPENDIX	THE DETERMINATION OF BISMUTH AND TELLURIUM IN SULPHIDE CONCENTRATES BY LIQUID-LIQUID EXTRACTION AND ATOMIC-ABSORPTION SPECTROPHOTOMETRY (LABORATORY METHOD NO. 76/3)	12
Table I-1	Amount of sample required	16

## LIST OF ILLUSTRATIONS

Figure 1	Variation in the extraction of bismuth with molarity of the nitric acid medium	9
Figure 2	Variation in the extraction of bismuth with equilibration time	9
Figure 3	Variation in the extraction of bismuth with volume of EDTA-Na <sub>4</sub>	10
Figure 4	Variation in the extraction of bismuth with volume of reagent solution	10
Figure 5	Variation in the extraction of bismuth with ratio of benzene to chloroform	11

## 1. INTRODUCTION

The analyses, by existing analytical techniques, of sulphide flotation concentrates for trace elements from groups V A and VI A (namely, arsenic, antimony, bismuth, selenium, and tellurium) is often difficult. For most of these elements, both emission spectrography and atomic-absorption spectrophotometry have poor sensitivity. In addition, the preparation of standards is lengthy, and, if atomic absorption is used, there is the possibility of interference from high concentrations of salt and metal ions during the direct measurement of solutions. The third-phase liquid-liquid-extraction technique developed by Zhivopistsev *et al.*<sup>1</sup> offers a procedure for the quantitative removal of trace amounts of metals from a bulk base-metal matrix, and simultaneous achievement of a high degree of concentration. The National Institute for Metallurgy (NIM) has successfully applied such a technique to the analysis of nickel-plating solutions<sup>2</sup>.

If this technique was to be applied to the analysis of sulphide concentrates, it was evident that considerable modification would be necessary before it could be adopted. The major constituents of the very diverse metal matrices, e.g., copper and lead, would also react with ligands like thiocyanate and iodide as used by Busev *et al.*<sup>3</sup> in the formation of the third phase and of complexes of the trace elements. However, they gave a method for the extraction of zirconium and hafnium into a third phase from nitric acid, presumably as nitro-complexes, and stated, without giving experimental details, that bismuth behaved similarly. An advantage of a nitric acid medium is the high solubility of lead, which is often present in sulphide concentrates. Busev and Babenko<sup>4</sup> extracted tellurium as a bromo-complex into dichloroethane from hydrobromic acid using a normal two-phase system. A third phase did not form in the presence of hydrobromic acid, but did form in the presence of perchloric acid, in which, as in nitric acid, base metals are highly soluble. In this medium, it is possible for tellurium to be reduced to the tetravalent state, in which form it can be extracted into a third phase.

The extraction of other group V A elements with bismuth was not possible in the nitric acid system. In addition, these elements do not form bromo-complexes under the conditions used for tellurium and consequently were not extracted into a third phase from perchloric acid. Under reducing conditions in perchloric acid, selenium precipitated as the element before a bromo-complex could be formed.

This report covers the investigations into the extraction of bismuth into a third phase from a nitric acid medium, the formation of a tellurium-bromide complex, and its subsequent extraction into a third phase, diantipyrylmethane (DAM) being used as the extracting agent. The application of the technique to the determination of bismuth and tellurium in sulphide concentrates is also examined.

## 2. EXPERIMENTAL METHOD

The formation of a third phase from 3 M nitric acid and 3 M perchloric acid with DAM was shown to occur reproducibly.

The formation of the extractable hexa-bromo-complex of tellurium occurs only when tellurium is in the tetravalent state. The reduction of tellurium must be achieved without the reduction of copper to its monovalent state, which would then precipitate as cuprous bromide. It was found possible to reduce tellurium with hydroxylamine hydrochloride as the reducing agent in perchloric acid at 70 °C.

After these essential preliminary facts had been established, the extraction of these two elements was considered in detail.

### 2.1. EXTRACTION OF BISMUTH AND TELLURIUM

Initial tests showed that the extraction of these elements from nitric or perchloric acid was dependent on the molarity of the aqueous phase, the time taken for equilibration, and the volume of the aqueous and third phase. Accordingly, these factors were studied in detail.

#### 2.1.1. Effect of Acidity

The optimum acidity for the extraction of bismuth (200 µg) and tellurium (100 µg) was ascertained by determination of the recovery\* from 1 to 6 M nitric acid and 2.5 to 5.8 M perchloric

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

## ANALYSIS OF BISMUTH AND TELLURIUM

acid respectively. For bismuth, 5 ml of 70 to 30 benzene-chloroform mixture containing 50 g of DAM per litre was added to 10 ml of the sample solution and equilibrated for 25 minutes. The tellurium was first reduced to the tetravalent state; 20 ml of perchloric acid, 0,8 g of hydroxylamine hydrochloride, and 2 g of sodium bromide were added to a solution containing 100 µg of tellurium, which was then heated at 70 to 75 °C. After it had cooled, the solution was transferred to a separating funnel, the aqueous volume was adjusted to 25 ml, 10 ml of 30 to 70 benzene-chloroform mixture containing 50 g of DAM per litre was added, and the solution was equilibrated for 10 minutes.

In each instance, the third phase was separated, was made up to 10 ml with methanol (for bismuth), or methanol containing 10 per cent (v/v) perchloric acid (for tellurium), and was determined by atomic-absorption spectrophotometry<sup>5</sup> with the use of an air-acetylene flame. The results were compared with standards that had been prepared by addition of the individual element to a blank extract. This procedure was adopted for all the subsequent tests. The results are given in Figure 1 (bismuth) and Table 1 (tellurium).

TABLE 1

*Extraction of the tellurium--bromide complex from a perchloric acid medium*

Acidity of complex formation M	Acidity of extraction M	Third-phase extraction %	Comments
2,5	2,5	Nil	
3,0	3,0	70,0	Non-viscous third phase Third phase slightly viscous and difficult to separate
3,5	3,5	82,4	
4,0	4,0	N.D.	Very viscous third phase, which was incompletely separated
5,8	5,8	N.D.	The yellow $\text{TeBr}_6^{2-}$ was formed, but Te could not be determined in the third phase because of high viscosity
3,5	3,0	81,0	Non-viscous third phase

N.D. = Not detected

A maximum extraction for bismuth of only 52 per cent was obtained at a molarity of 3,5, the extraction for tellurium being 82,4 per cent from 3,5 M perchloric acid. At higher molarities, the viscous nature of the third phase that formed prevented quantitative recovery of this phase, extraction having occurred. At a molarity of 2,5 or less, the tellurium-bromide complex was not formed. Therefore, the conditions of extraction adopted for tellurium were the formation of the bromide complex in 3,5 M perchloric acid and dilution to 3,0 M before extraction.

### 2.1.2. Equilibration Time

The variation of recovery with time was examined for both elements, the conditions given in Section 2.1.1 being used, and the time of contact varying from 0 to 20 minutes (see Figure 2).

The extraction of bismuth decreased slowly with time from 54 to 48 per cent, whereas that of tellurium remained constant after 5 minutes, the extraction being in the region of 80 per cent. For improvement of the extraction of bismuth, an attempt was made to form an acid-stable anionic complex of ethylenediaminetetra-acetic acid (EDTA) by the addition of a 5 per cent EDTA solution.

## ANALYSIS OF BISMUTH AND TELLURIUM

With the addition of 0,25 ml of EDTA solution, recoveries improved from 52 to 65 per cent (see Figures 2 and 3), and remained constant with time, no darkening of the third phase with time being observed. It was concluded that the nitration reaction<sup>6</sup> had been inhibited. Equilibration times of 5 and 10 minutes were therefore adopted for bismuth and tellurium respectively.

### 2.1.3. Effect of Varying Phase Ratios

The volume of the third phase produced bears an almost linear relation to the volume of the reagent solution used<sup>7</sup>. Therefore, the variation in the extraction of bismuth with volume of reagent added (synonymous with the volume of the third phase) was examined for varying additions to a constant (10 ml) volume of aqueous phase. A linear increase in extraction was observed (see Figure 4) with increasing addition of reagent, indicating that a normal distribution law is obeyed and that there is only one extractable species. Additions larger than 15 ml would give a third phase, which, in a final volume of 10 ml, would be insufficiently diluted with methanol to give suitable atomic-absorption measurements.

Similar tests were not carried out for tellurium, the assumption being made that increased additions of reagent would in the same way improve the extraction above the 82 per cent already recorded.

### 2.1.4. Effect of Diluent Composition on Extraction

As the extraction parameters discussed so far give conditions of extraction differing from those quoted by Busev<sup>3</sup>, it was decided that examination of the composition of the diluent would be advisable. The ratio of benzene to chloroform plays an important part in the fractionation of the organic phase.

The effects of variation in the ratio of benzene to chloroform between 80 to 20 and 20 to 80 are shown in Figure 5 for bismuth and Table 2 for tellurium. The optimum ratio for bismuth appears to be 60 to 40, although extractions greater than 80 per cent were obtained within a range of ratios of benzene to chloroform between 65 to 35 and 50 to 50. The use of a ratio of 60 to 40 allows for the addition of more chloroform as a wash solution without the risk of back-extraction. An increase in the chloroform content of the diluent increases the density of the third phase and improves separation. For tellurium, it is evident from Table 2 that the third phase is formed from a 3 M perchloric acid medium only when the ratio of benzene to chloroform of 30 to 70 (as in previous tests) is used, and that variations in the composition of the diluent do not improve the extraction of tellurium.

TABLE 2

*Third-phase formation in the presence of perchloric acid*

Ratio of benzene to chloroform	Comments on the third phase
70-30	Solid
50-50	Solid
40-60	Liquid, slightly turbid
35-65	Liquid, slightly turbid
30-70	Liquid, clear
25-75	Liquid, smaller volume than above phases
20-80	None

## 2.2. CO-EXTRACTION OF MATRIX ELEMENTS

So that the possibility of the co-extraction of copper, lead, zinc, and iron (i.e., the major constituents of sulphide concentrates) would be avoided, it was decided to take an aliquot portion of the leach liquor of a 1 g sample that would be the equivalent of 0,1 g of sample and still have an adequate sensitivity for the determination of bismuth and tellurium. An aliquot like this would contain 30, 75, 55, 30, and 300 milligrams of copper, lead, zinc, iron, and sodium respectively. The co-extraction of these elements and the recovery of bismuth in their presence were tested in higher

## ANALYSIS OF BISMUTH AND TELLURIUM

amounts than these, namely, 150, 100, 300, 150, and 270 milligrams respectively, 100  $\mu\text{g}$  of bismuth also being present (see Table 3).

**TABLE 3**

*Co-extraction of matrix elements and extraction of bismuth in their presence*

Amount of bismuth : 100  $\mu\text{g}$

Matrix	Mass added mg	Extraction, %		Relative difference %
		Matrix element	Bi	
Nil	Nil	—	84,9	—
Cu	150	0,05		
Pb	100	0,25	83,5	— 1,4
Zn	300	0,05		
Fe	150	2,5	83,0	— 1,9
Cu+Zn	150 + 300		82,0	— 2,9
Na	270	< 0,01		
NaNO <sub>3</sub>	1000		96,0	+ 11,1
Na <sub>2</sub> SO <sub>4</sub>	1000		96,0	+ 11,1
Fe, Cu	30,50			
Zn, Na	50,1000		No Recovery	

It is evident that only iron shows any significant degree of co-extraction (2,5 per cent) and that, with the exception of sodium, the metals present individually or in combination do not affect the extraction of bismuth within the experimental error of the procedure.

The extracted iron formed an insoluble complex with the DAM and was allowed to settle before the atomic-absorption determinations, so that it had no effect on the measurements. However, when iron is present in combination with the other base metals and sodium, visual identification of the intermediate and heavy organic phases becomes difficult, and separation becomes virtually impossible. A significant improvement in extraction is observed when sodium ions are present because they have a salting-out effect.

As none of the matrix elements in sulphide concentrates that are under consideration forms bromo-complexes, co-extraction with tellurium is not to be expected.

However, the possibility that the presence of these elements would affect the extraction of tellurium was investigated as follows: 1 g of each concentrate was fused with 5 g of sodium peroxide after the silica had been removed with hydrofluoric acid; it was then leached with water and perchloric acid, and the acidity of the final solution (100 ml) was adjusted to 3,5 M perchloric acid; aliquot portions of 20 ml were taken, 20  $\mu\text{g}$  of tellurium was added, and the bromo-complex was formed and extracted according to the method given in the Appendix. The recoveries and percentages of co-extracted matrix elements are given in Table 4.

There is virtually no co-extraction of the base metals, but the presence of a relatively large amount of copper results, surprisingly, in an almost quantitative extraction — a phenomenon that was confirmed by further tests involving only tellurium and copper, in which the recoveries again exceeded 90 per cent compared with 72 per cent in the presence of less than 1 mg of copper. In the subsequent analysis of concentrate samples, sufficient copper was added to give at least 4 mg in the aliquot portion taken for analysis.

### 2.3. ELIMINATION OF INTERFERENCES IN THE DETERMINATION OF BISMUTH

In the analysis of samples of concentrate, it was observed that, in addition to the interference from iron, the presence of silica in concentrations greater than 2 per cent resulted in the formation of a

## ANALYSIS OF BISMUTH AND TELLURIUM

precipitate with the DAM. The silica was removed without loss of tellurium by evaporation of the nitric acid leach liquor with hydrofluoric and perchloric acids<sup>8</sup>. Direct treatment of the concentrate with hydrofluoric acid before fusion led to a loss of tellurium.

**TABLE 4**

*Co-extraction of matrix elements and extraction of tellurium in their presence*

Amount of tellurium : 20  $\mu$ g

Matrix	Mass present mg				Extraction, %				
					Matrix elements				
	Zn	Cu	Pb	Na	Fe	Cu	Pb	Zn	Te
Zn	100	1		1000	0,1	0,05	< 0,1	0,05	72,4
Pb			145	1000	< 0,1	0,05	0,15	< 0,01	71,0
Cu		54		1000	0,1	0,2	0,1	< 0,01	95,0
		4		1000					95,1
		8		1000					91,5
		16		1000					97,8

The interference from iron was eliminated by the addition of 0,25 ml of 40 per cent (v/v) thioglycolic acid, which formed a complex with iron and so prevented any precipitation of an iron-DAM complex, and enabled the two heavier phases to be identified and separated. However, the presence of thioglycolic acid reduced the extraction of bismuth from 97 to 90 per cent (see Table 5).

**TABLE 5**

*Effect of thioglycolic acid on the extraction of bismuth*

Amount of bismuth	20 $\mu$ g
Volume of aqueous phase	10 ml
Molarity of aqueous phase	3,5 M HNO <sub>3</sub>
Amount of NaNO <sub>3</sub>	1 g
Volume of thioglycolic acid	0,25 ml
Volume of 50 g/l EDTA-Na <sub>4</sub>	0,25 ml
Shaking time	5 min

Concentration of thioglycolic added % (v/v)	Extraction %
None	97,0
40	90,0
50	90,2

## ANALYSIS OF BISMUTH AND TELLURIUM

### 3. PROCEDURE

The procedure adopted for the sequential determination of bismuth and tellurium is given in the Appendix. Compensation for the incomplete extractions is made by the spiking of portions of the sample solution before extraction and determination of the unknown concentration by the method of standard additions.

### 4. APPLICATION TO THE ANALYSIS OF SULPHIDE CONCENTRATES

In the absence of recognized standard reference materials, an evaluation of the accuracy of the procedure as applied to copper, lead, and zinc sulphide concentrates was made by a comparison with data obtained by alternative procedures, where these were applicable, i.e., data resulting from the use of atomic-absorption spectrophotometry, atomic-absorption spectrophotometry coupled with hydride generation, atomic-absorption spectrophotometry coupled with concentration by co-precipitation, and emission spectrography.

Three determinations for bismuth were made on the copper and zinc concentrates and six on the lead concentrate, and two determinations were made for tellurium. The mean values are given in Table 6. The precision of the method for bismuth and tellurium was determined from six measurements, the lead concentrate (OPO 647/2) being used for bismuth, and eight measurements being made on the copper concentrate spiked with 100  $\mu\text{g}$  of tellurium before fusion. The coefficients of variation were 3,0 and 3,8 per cent respectively.

The agreement for bismuth is good. The comparison for tellurium is limited by the fact that direct procedures are insensitive to this element and a value is obtained only when a concentration step is included. If the difficulties associated with the analysis of tellurium are considered, the agreement between the two sets of values that are available is reasonable.

### 5. DISCUSSION

The advantages of the three-phase separation for bismuth and tellurium over existing methods are its speed and its applicability to matrices containing a wide variety of base metals. The tellurium extraction is particularly useful in this respect since it is specific. When the sample fusion can be leached direct with perchloric acid and tellurium extracted into the third phase and determined by atomic absorption, this analysis can be carried out in about two hours. Another advantage of this separation technique is that it permits the use of other sensitive analytical finishes, which cannot often tolerate the presence of interfering elements to any extent. The carbon-rod atomizer is one such technique, and the limit of determination of bismuth and tellurium could be extended down to 0,1 p.p.m. The precision obtainable is better in acid than in organic media, and it has been shown that the third phase can be dissolved in either 40 per cent (v/v) sulphuric or nitric acid. The extraction coupled with the use of a carbon-rod atomizer should offer better sensitivity for many elements than that offered by the procedure used by Busev *et al.*<sup>3</sup>. Busev's procedure involves quantitative transfer of the small volume of third phase to an electrode and subsequent use of spark excitation, which lacks sensitivity for many elements.

Elements forming hydrides, e.g., tellurium, can be determined by hydride generation coupled with atomic-absorption spectrophotometry. In its three-phase separation, tellurium is in the appropriate oxidation state (tetravalent) for the generation of the hydride, which is not always so when other cations are present.

A salting-out effect, which causes a great improvement in the extraction, is often very important in these extractions, particularly for bismuth in the presence of sodium nitrate. Other third-phase extractions, such as those made by Busev from thiocyanate media, are affected similarly, and significant differences in extraction have been observed in this laboratory between the results obtained with sodium, potassium, and ammonium salts respectively, a factor not discussed by the Russian workers. The extraction of tellurium is not affected significantly by sodium salts but is much improved when copper is present. It is possible that this improvement is caused by the presence of the free bromine formed during the complexing of tellurium and sodium bromide.

### 6. CONCLUSION

Bismuth and tellurium can be almost quantitatively extracted from the third phase of a liquid-liquid-extraction system containing DAM and acid: nitric acid for bismuth and perchloric acid for tellurium. This scheme has been applied to the analysis of sulphide concentrates having matrices of

ANALYSIS OF BISMUTH AND TELLURIUM

TABLE 6

Comparative analyses of sulphide concentrates

Element	Concentrate	Atomic-absorption spectrophotometry			Emission spectroscopy	
		Three-phase extraction p.p.m.	Hydride generation p.p.m.	Direct determination with standard additions p.p.m.	Induction-coupled plasma p.p.m.	Direct-current arc p.p.m.
Bi	Copper 33/74	335		341	354	57
	Zinc 31/74	60	65	65		
	Lead OPO/647/2	1290		1297		
Te	Copper 33/74	< 10	0,2			
	Zinc 31/74	< 10	3,7			
	Lead 32/74	< 10	4,9			

## ANALYSIS OF BISMUTH AND TELLURIUM

different metals, compensation for the extraction being made by spiking of the solutions before extraction.

During the extraction of bismuth, high concentrations of iron were successfully masked with thioglycolic acid. Although high in the third phase, the concentration factors are low (1 to 2) in the final solution for analysis. However, separation from interfering elements (with the exception of iron, which forms a complex) and an enhancement of 2 to 3 in absorbance are attained if a methanol medium is used. The lower limit of determination by conventional atomic-absorption measurement is 20 p.p.m. for bismuth and 10 p.p.m. for tellurium in sulphide concentrates. The coefficient of variation for bismuth at the 1000 p.p.m. level is 3 per cent and, for tellurium at the 100 p.p.m. level, 3,8 per cent.

### 7. REFERENCES

1. ZHIVOPISTSEV, V.P., *et al.* *Zh. analyt. Khim.*, vol. 18. 1963. p. 1432.
2. MALLET, R.C., NICOLAS, D.J., BUULTJENS, J., and STEELE, T.W. The analysis of nickel-refining solutions: separation of trace elements by liquid-liquid extraction followed by atomic-absorption measurement. National Institute for Metallurgy, Johannesburg, *Report no. 1688*. 29th Nov., 1974.
3. BUSEV, A.I., *et al.* Spektral chemische analysenmethoden unter benutzung der drephasen systeme der extraktion. *Talanta*, vol. 19. 1972. p. 173.
4. BUSEV, A.I., and BABENKO, N.L. Pyrazolone derivatives as reagents for tellurium. *J. analyt. Chem. USSR*, vol. 14. 1965. p. 842.
5. VARIAN TECHTRON MANUAL. Analytical methods for flame spectroscopy.
6. ZHIVOPISTSEV, V.P., *et al.* *Zavod. Lab.*, vol. 35. 1969. p. 902.
7. NICOLAS, D.J., and STEELE, T.W. The application of three-phase liquid-liquid extraction to the separation and concentration of noble metals. National Institute for Metallurgy, Johannesburg, *Report no. 1684*. 5th Dec., 1974.
8. NAZARENKO, I.I., and ERMAKOV, A.N. Analytical chemistry of selenium and tellurium. London, Wiley, 1972. pp. 196-198.

ANALYSIS OF BISMUTH AND TELLURIUM

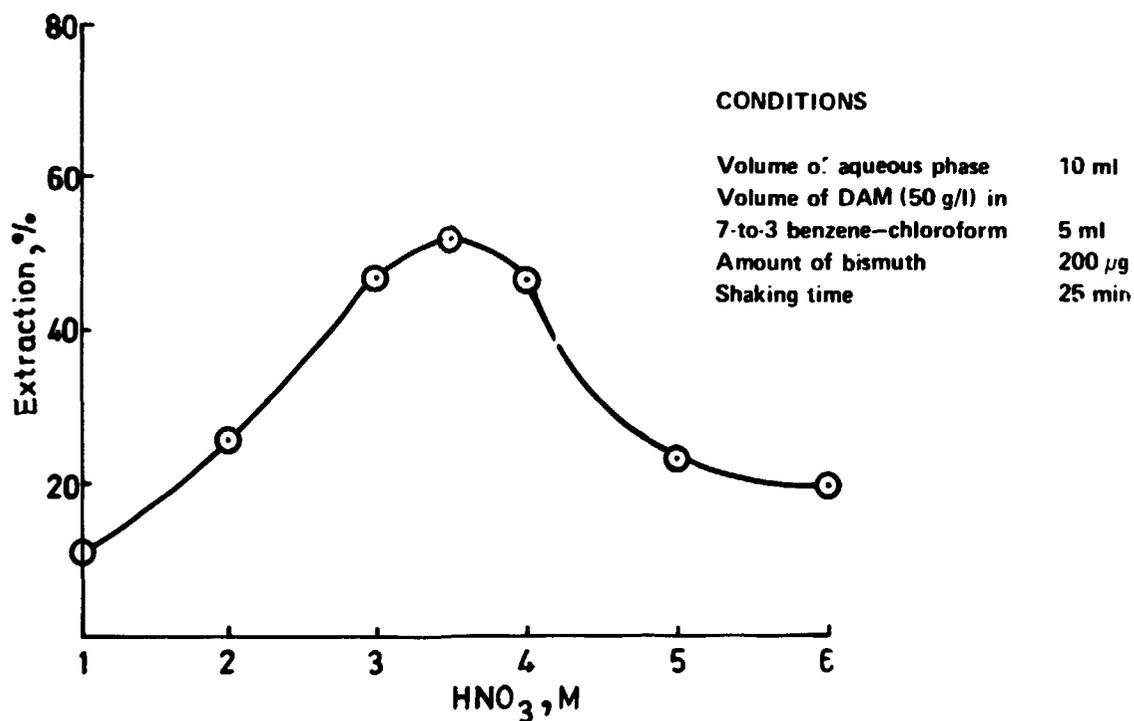


FIGURE 1 Variation in the extraction of bismuth with molarity of the nitric acid medium

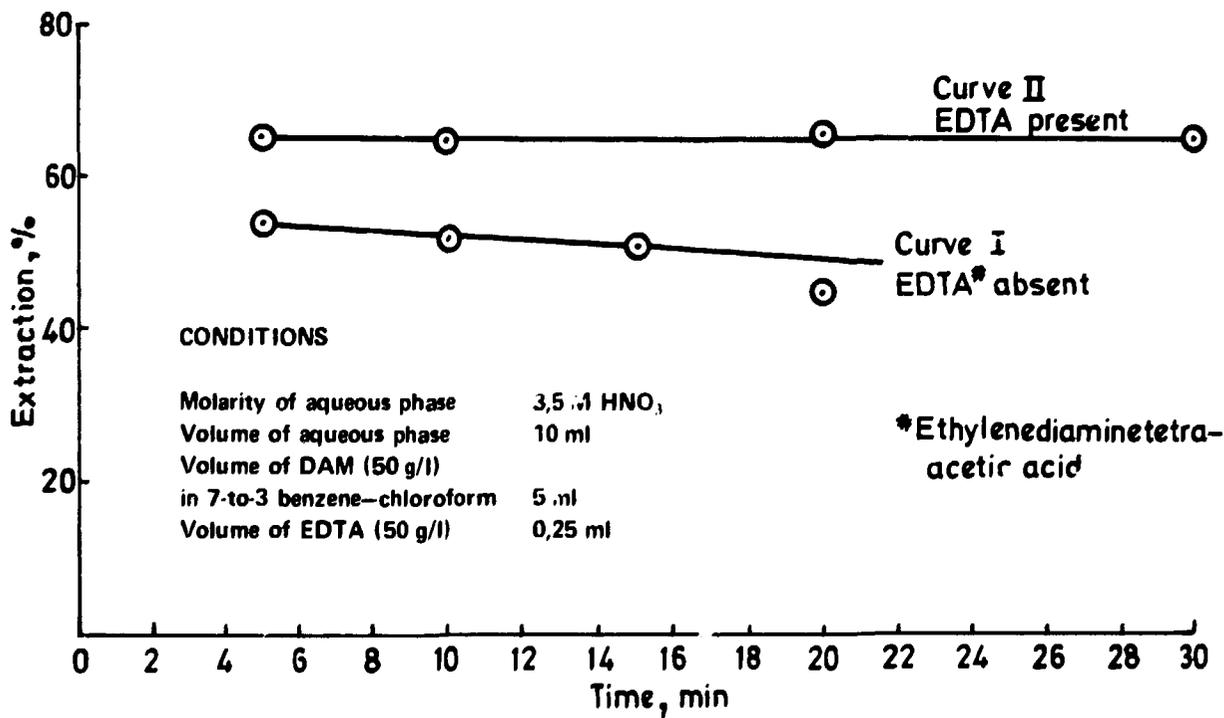


FIGURE 2 Variation in the extraction of bismuth with equilibration time

ANALYSIS OF BISMUTH AND TELLURIUM

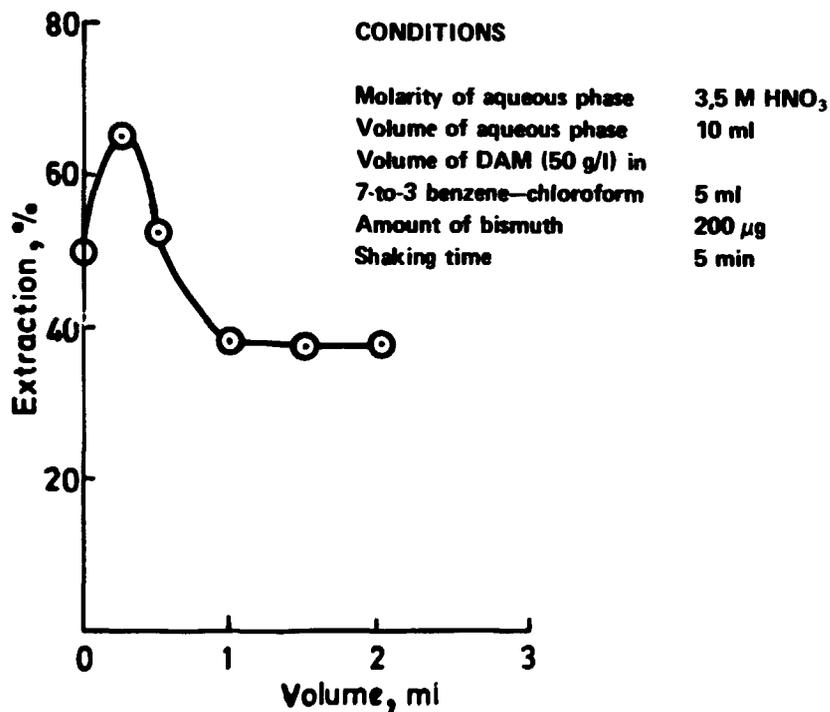


FIGURE 3 Variation in the extraction of bismuth with volume of EDTA-Na<sub>4</sub>

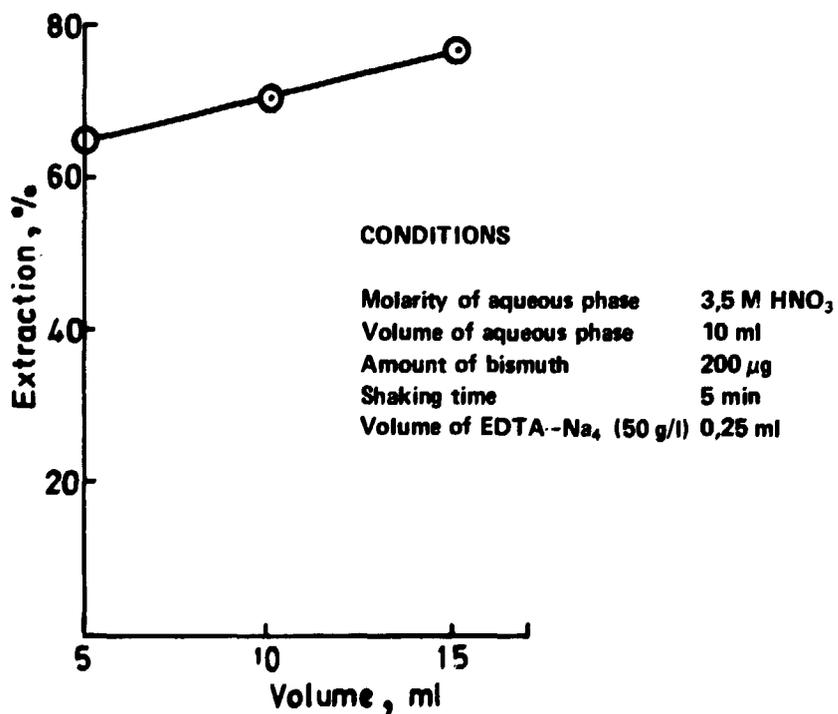


FIGURE 4 Variation in the extraction of bismuth with volume of reagent solution

# ANALYSIS OF BISMUTH AND TELLURIUM

## CONDITIONS

Molarity of aqueous phase 3,5 M HNO<sub>3</sub>  
Volume of aqueous phase 10 ml  
Volume of DAM (50 g/l) 15 ml  
Amount of bismuth 200 μg  
Shaking time 5 min  
Volume of EDTA-Na<sub>4</sub> (50 g/l) 0,25 ml

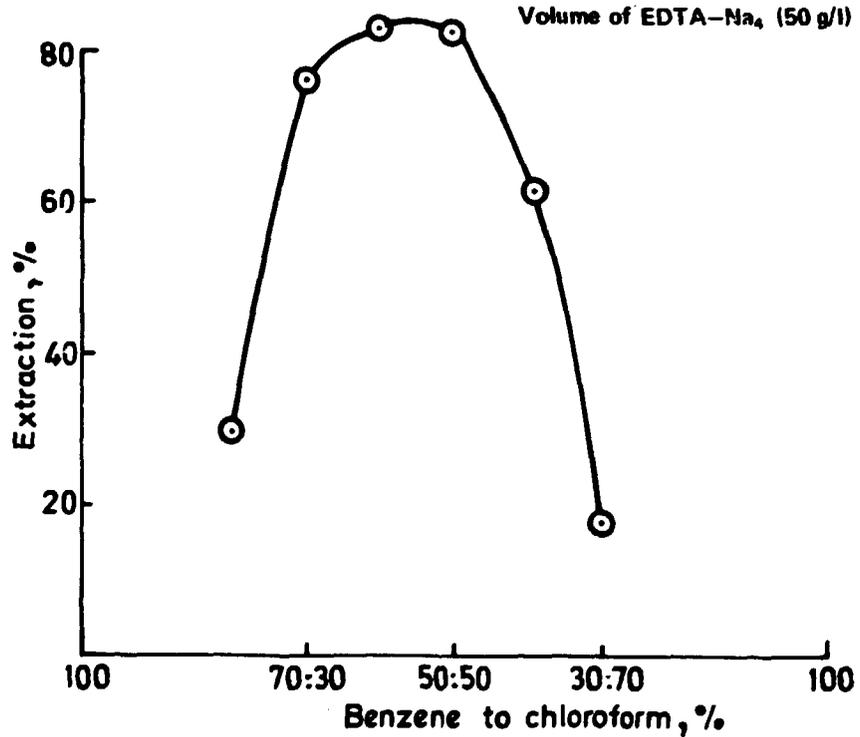


FIGURE 5 Variation in the extraction of bismuth with ratio of benzene to chloroform

# ANALYSIS OF BISMUTH AND TELLURIUM

E.1. Bismuth  
E.1. Tellurium

## APPENDIX

### THE DETERMINATION OF BISMUTH AND TELLURIUM IN SULPHIDE CONCENTRATES BY LIQUID-LIQUID EXTRACTION AND ATOMIC-ABSORPTION SPECTROPHOTOMETRY (LABORATORY METHOD NO. ~~753~~ 8/3)

#### 1. OUTLINE OF THE METHOD

A sulphide concentrate is fused with a mixture of sodium peroxide and sodium carbonate in a nickel crucible. The melt is leached with water and nitric acid and made up to volume. Aliquot portions of the leach liquor are transferred to separating funnels, bismuth additions are made, and bismuth is extracted into a third phase formed on the addition of a benzene-chloroform-diantiprylmethane mixture. Other aliquot portions are taken, and, after conversion of the medium from nitric acid to perchloric acid, tellurium additions are made. The tellurium forms a complex and is extracted into a third phase. If it is necessary to remove silica (i.e., if the silica content is greater than 2.0 per cent), a hydrofluoric acid-nitric acid evaporation is made after the fusion and before the spiking. After dilution with methanol, bismuth and tellurium are determined in their respective separated third phases by atomic-absorption spectrophotometry. The technique of standard additions compensates for incomplete extraction and for any interferences with the atomic-absorption determination.

#### 2. APPLICATION OF THE METHOD

The method is applicable to the determination of bismuth and tellurium in sulphide flotation concentrates that can be taken into solution by fusion with sodium peroxide and sodium carbonate and leaching with acid.

The limits of determination by flame atomic-absorption measurement of the third-phase organic extracts are 20 p.p.m. for bismuth and 10 p.p.m. for tellurium.

#### 3. REAGENTS

- (1) *Hydrofluoric Acid*  
A.R. grade, sp.gr. 1,2
- (2) *Nitric Acid*  
A.R. grade, sp.gr. 1,39
- (3) *Nitric Acid, 3,5 M*  
Dilute 250 ml of A.R.-grade nitric acid (sp.gr. 1,39) to 1000 ml with distilled water.
- (4) *Perchloric Acid*  
A.R. grade, sp.gr. 1,67
- (5) *Perchloric Acid, 3,5 M*  
Dilute 300 ml of A.R. grade perchloric acid (sp.gr. 1,67) to 1000 ml with distilled water.
- (6) *Chloroform*  
A.R. grade
- (7) *Benzene*  
A.R. grade
- (8) *Methanol*  
A.R. grade
- (9) *Methanol-Nitric Acid Solution*  
Add 10 ml of nitric acid (sp.gr. 1,39) to 90 ml of methanol.
- (10) *Methanol-Perchloric Acid Solution*  
Add 10 ml of perchloric acid (sp.gr. 1,67) to 90 ml of methanol.
- (11) *Hydrogen Peroxide*  
A.R. grade  $H_2O_2$ , 300 g/l
- (12) *Sodium Peroxide*  
A.R. grade

## ANALYSIS OF BISMUTH AND TELLURIUM

- (13) *Sodium Carbonate*  
A.R. grade
- (14) *Sodium bromide*  
A.R. grade
- (15) *Hydroxylamine Hydrochloride*  
A.R. grade
- (16) *Solution A for Bismuth, 4,4' Diantipyrilmetbane (DAM), 50 g/l*  
Dissolve 5 g of DAM in a mixture of 6 parts benzene and 4 parts chloroform (v/v), and make it up to 100 ml with the benzene-chloroform mixture.
- (17) *Solution B for Tellurium, 4,4' DAM, 50 g/l*  
Dissolve 5 g of DAM in a mixture of 3 parts benzene and 7 parts of chloroform (v/v), and make it up to 100 ml with the benzene-chloroform mixture.
- (18) *Ethylenediaminetetra-acetic Acid (EDTA)-Na<sub>4</sub> Solution, 50 g/l*  
Dissolve 5 g of A.R.-grade EDTA-Na<sub>4</sub> in distilled water and make up to 100 ml.
- (19) *Thioglycolic Acid Solution, 40 % (v/v)*  
Dilute 40 ml of A.R.-grade thioglycolic acid (800 g/l) to 100 ml with distilled water.
- (20) *Copper Sulphate Solution, 10 g/l*  
Dissolve 3.9 g of A.R.-grade copper sulphate (CuSO<sub>3</sub>.5H<sub>2</sub>O) in distilled water, add 30 ml of perchloric acid (sp.gr. 1,67), and make up to 100 ml with distilled water.
- (21) *Stock Bismuth Solution*  
Dissolve 0,580 g of A.R.-grade bismuth nitrate (Bi(NO<sub>3</sub>)<sub>3</sub>.5H<sub>2</sub>O) in 3,5 M nitric acid and make up to 500 ml with 3,5 M nitric acid.

1 ml  $\equiv$  1 mg of Bi.

- (22) *Stock Tellurium Solution*  
Dissolve 0,900 g of A.R.-grade telluric acid (H<sub>2</sub>TeO<sub>4</sub>.2H<sub>2</sub>O) in 3,5 M perchloric acid, and make up to 500 ml with 3,5 M perchloric acid. Warm slightly to dissolve.

1 ml  $\equiv$  1 mg of Te.

- (23) *Working Standard Solutions*  
In separate volumetric flasks, dilute 5 and 10 ml each of the stock solutions of bismuth and tellurium to 100 ml with 3,5 M nitric and perchloric acids respectively.

1 ml  $\equiv$  100  $\mu$ g of Bi or Te

1 ml  $\equiv$  50  $\mu$ g of Bi or Te.

### 4. PROCEDURE

#### 4.1. CALIBRATION

Calibration is effected by the technique of standard additions. One aliquot portion of the respective sample solution is not spiked, and further aliquot portions are spiked with varying amounts of analyte and measured by atomic-absorption spectrophotometry. Normally, two aliquot portions are spiked, but three may be required if the linearity of the calibration is to be checked. An account of this technique and a guide to the number and metal content of the additions that should be made are given in the Varian-Techtron handbook<sup>1</sup>.

#### 4.2. AMOUNT OF SAMPLE

The amounts of sample required for sulphide concentrates are shown in Table I-1.

#### 4.3. DISSOLUTION OF THE SAMPLE

- Transfer an appropriate amount of sample (see Table I-1) to a nickel crucible to which 1 g of sodium carbonate has been added.
- Add 4 g of sodium peroxide, mix the contents of the crucible, and sinter over a Bunsen burner to oxidize the sulphur without ignition (Note 1).
- Fuse the residue at a dull-red heat until a clear melt is obtained. Cool the crucible.
- Place the crucible in a 150 ml beaker, and add 15 ml of water. Cover the beaker with a watch-glass, and allow the reaction to cease.
- Cautiously add 10 ml of nitric acid (sp.gr. 1,39) to the crucible.

## ANALYSIS OF BISMUTH AND TELLURIUM

- f. After the melt has been completely leached, transfer the crucible contents plus washings to the beaker.
- g. Adjust the pH value to 1 (using Universal indicator paper), with further drop-by-drop additions of acid if necessary, and then add sufficient nitric acid (sp.gr. 1,39) to bring the molarity to 3,5 (Note 2).
- h. Heat this solution on a hot-plate, and add hydrogen peroxide drop by drop while stirring until complete dissolution occurs.
- i. Cool, transfer to a volumetric flask (see Table I-1), and dilute to volume.
- j. Take three aliquot portions of each solution (see Table I-1), and remove the silica if necessary as described in Note 3(a).
- k. To two aliquot portions add increasing amounts of bismuth, depending on the estimated value in the sample.
- l. Extract these solutions as described in Section 4.4.1.
- m. Take a further three aliquot portions for the determination of tellurium (see Table I-1) and pipette these aliquot portions into 100 ml beakers, add 7,5 ml of perchloric acid (sp.gr. 1,67), and evaporate the nitric acid off until five minutes after fumes of perchloric acid appear.
- n. If necessary, remove the silica and nitric acid as described in Note 3(b). To two aliquot portions add increasing amounts of tellurium, depending on the estimated value in the sample.
- o. Extract these solutions as described in Section 4.4.2.

### 4.4. EXTRACTION

#### 4.4.1. Bismuth

- a. Extract concurrently at least three aliquot portions for each sample (see Section 4.1.). Transfer these portions to 100 ml separating funnels.
- b. Add 0,25 ml of EDTA- $\text{Na}_4$  solution and, if the aliquot portion contains more than 10 mg of iron, add 0,25 ml of (v/v) thioglycolic acid.
- c. Spike the solutions in the funnels with an appropriate amount of bismuth working solution not exceeding 1 ml (see Section 4.1). Add the same volume of 3,5 M nitric acid to the solution that has not been spiked.
- d. Add 15 ml of DAM solution A and shake for 5 minutes. Allow the third phase to settle out.
- e. Run the third phase out (see Note 4), and make up to volume with methanol-nitric acid solution (see Table I-1).

#### 4.4.2. Tellurium

- a. Extract concurrently at least three aliquot portions for each sample (see Section 4.1). Transfer the perchloric acid solutions (see steps m, n, and o of Section 4.3) to 100 ml beakers with distilled water, and adjust the volume to 20 ml.
- b. If an aliquot portion contains less than 4 mg of copper, add 0,4 ml of the copper sulphate solution.
- c. Spike the solutions in the beakers with an appropriate amount of tellurium working solution not exceeding 1 ml (see Section 4.1). Add the same volume of 3,5 M perchloric acid to the solution that has not been spiked.
- d. Add 2 g of sodium bromide and 0,8 g of hydroxylamine hydrochloride.
- e. Heat on a steam-bath for 15 minutes at  $75^\circ\text{C} \pm 5^\circ\text{C}$ .
- f. Transfer to separating funnels with distilled water, and adjust the aqueous volume to 25 ml.
- g. If less than 30 mg of copper is present, add 10 ml of DAM solution B. If 30 mg of copper or more is present, add 15 ml. Shake for 10 minutes. Allow the third phase to settle out.
- h. Run the third phase out (see Note 4), and make up to volume with methanol-perchloric acid solution (see Table I-1).

### 4.5. ATOMIC-ABSORPTION MEASUREMENT

Use the instrumental parameters for the Varian-Techtron atomic-absorption spectrophotometer as given in their handbook<sup>1</sup> (Note 5). The most sensitive resonance lines and an air-acetylene flame are used for the determination of bismuth and tellurium. Background is determined by the measurement of solution absorbance with a hydrogen-continuum lamp, but is usually negligible at low scale expansions.

## ANALYSIS OF BISMUTH AND TELLURIUM

### 5. CALCULATION

Let  $X$  = Bi or Te in third phase ( $\mu\text{g}$ )  
 $a$  = Bi or Te added before extraction ( $\mu\text{g}$ )  
 $A_1$  = absorbance of third-phase solution that is not spiked  
 $A_2$  = absorbance of third-phase solution that is spiked

Then

$$\frac{X}{X+a} = \frac{A_1}{A_2} \quad (1)$$

Therefore, Bi or Te in sample (p.p.m.)

$$= X \times \frac{\text{volume of leach liquor (ml)}}{\text{aliquot portion taken for extraction (ml)}} \times \frac{1}{\text{mass of sample (g)}} \quad (2)$$

If two additions are made, calculate two values of  $X$  using equation (1) and average them. If more than two additions are made, calculate  $X$  graphically.

### 6. NOTES

- (1) If the sulphur ignites, the resulting violent exothermic reaction can cause the sample to spit.
- (2) A 3,5 M nitric acid solution requires 25 ml of nitric acid (sp.gr. 1,39) to be added to the solution, which has a pH value of 1 and is diluted to a volume of 100 ml.
- (3) If the removal of silica is necessary (when the silica content is more than 2 per cent), the following procedure is adopted.
  - (a) For bismuth, evaporate aliquot portions of the leach liquor (see Table I-1) in platinum dishes with 10 ml of hydrofluoric acid to incipient dryness. Add 10 ml of 3,5 M nitric acid and 5 ml of hydrofluoric acid, and repeat the evaporation. Add 10 ml of nitric acid and make a final evaporation. Redissolve the salts with 5 ml of 3,5 M nitric acid and transfer to separating funnels, washing out any residues with 5 ml of 3,5 M nitric acid.
  - (b) For tellurium, evaporate aliquot portions of the leach liquor (see Table I-1) in platinum dishes with 7,5 ml of perchloric acid (sp.gr. 1,67) and 10 ml of hydrofluoric acid until fumes of perchloric acid appear. Take care that salts do not precipitate. Add 10 ml of 3,5 M nitric acid and repeat the evaporation. Transfer to 100 ml beakers with distilled water, and adjust the volume to 20 ml. Form the complexes and do the extraction as described in Section 4.4.2.
- (4) Run off the third phase, usually the lowest, as completely as possible, and rinse the stem with methanol-acid solution. If the third phase forms above the aqueous phase, run the latter off first, and rinse the stem with methanol before removing the third phase. Use chloroform (about 2 ml) for washing the two remaining phases in the separating funnel and its walls, swirling the phases very gently. After 5 minutes of settling, run off a few drops of the bottom phase, which will contain some third phase collected from the walls and interface between the phases, and add this to the third phase. Make the third phase up to volume with the methanol-acid solution (see Table I-1).
- (5) Solutions containing the third phase and methanol are best nebulized with the use of a support pressure of approximately 100 kPa. This is lower than that recommended by the manufacturer if a fixed nebulizer is used. However, better control of the nebulization process can be attained if a variable nebulizer is used, which allows the nebulization of more viscous solutions than those recommended here (see Table I-1).

### 7. REFERENCE

1. VARIAN-TECHTRON. Analytical methods for flame spectroscopy.

## ANALYSIS OF BISMUTH AND TELLURIUM

TABLE I-1

*Amount of sample required*

Metal	Estimated amount of metal p.p.m.	Mass of sample to be taken g	Volume of leach liquor ml	Aliquot portion for extraction ml	Final volume for measurement ml
Bi	20 to 100	1,0	50	10	10
Bi	100 to 500	1,0	100	10	10
Bi	500 to 1000	0,5	100	10	15
Bi	1000 to 1500	0,5	100	10	20
Te	10 to 100	1,0	100	20	10
Te	100 to 500	1,0	100	20	10