REPORT NO. 1857
THE DETERMINATION OF SOME TRACE ELEMENTS IN SULPHIDE CONCENTRATES BY SPECTROPHOTOMETRY

Director of Division T.W. Steele

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SYNOPSIS

The report describes the determination of trace amounts (as low as 1 to 10 p.p.m. depending on the element) of arsenic, germanium, molybdenum, nickel, phosphorus, selenium, tellurium, tin, and titanium in sulphide concentrates. The proposed methods, which are detailed in the appendices, are adaptations of established procedures that were modified to allow for the complex nature of the concentrates to be analysed.

SAMEVATTING

Die verslag beskryf die bepaling van spoorhoeveelhede (so min as 1 tot 10 d.p.m. afhankende van die element) van arseen, germanium, molibdeen, nikkel, fosfor, seleen, telluur, tin en titaan in sulfiedkonsentrate. Die voorgestelde metodes, wat in die aanhangsels uiteengesit word, is aanpassings van gevestigde metodes wat gewysig is om voorsiening te maak vir die ingewikkelde aard van die konsentrate wat ontleed moet word.
CONTENTS

1. INTRODUCTION ................................................................. 1

2. DISSOLUTION PROCEDURES .................................................. 1

3. SEPARATION OF INDIVIDUAL ELEMENTS ................................. 1
   3.1. ARSENIC ................................................................. 1
   3.2. GERMANIUM .............................................................. 2
   3.3. MOLYBDENUM .......................................................... 2
   3.4. NICKEL ................................................................. 2
   3.5. PHOSPHORUS ............................................................ 2
   3.6. SELENIUM ............................................................... 2
   3.7. TELLURIUM .............................................................. 2
   3.8. TIN ................................................................... 3
   3.9. TITANIUM ............................................................... 3

4. APPLICABILITY OF THE PROCEDURES ADOPTED ......................... 3

5. CONCLUSIONS ................................................................... 3

6. REFERENCES ...................................................................... 3

Table 1 Summary of procedures .................................................. 5
Table 2 Evaluation of procedures adopted .................................... 6
Table 3 Comparison of results obtained by various methods of analysis 7

Appendix I The spectrophotometric determination of arsenic (laboratory method no. 33/9) .................................................. 8
Appendix II The spectrophotometric determination of germanium (laboratory method no. 32/1) ................................................... 10
Appendix III The spectrophotometric determination of molybdenum (laboratory method no. 42/6) ................................................... 12
Appendix IV The spectrophotometric determination of nickel (laboratory method no. 28/9) .......................................................... 15
Appendix V The spectrophotometric determination of phosphorus (laboratory method no. 15/16) ..................................................... 18
Appendix VI The fluorimetric determination of selenium (laboratory method no. 34/4) ................................................................. 21
Appendix VII The spectrophotometric determination of tellurium (laboratory method no. 52/1) .......................................................... 24
Appendix VIII The spectrophotometric determination of tin (laboratory method no. 50/9) ............................................................... 27
Appendix IX The spectrophotometric determination of titanium (laboratory method no. 22/12) ......................................................... 29
1. INTRODUCTION

The analytical requirements for trace and minor components in sulphide-ore concentrates depend on the origin of the ore-body and on smelter practice. These components comprise about 20 elements, 9 of which (arsenic, selenium, tellurium, germanium, tin, nickel, molybdenum, titanium, and phosphorus) are considered the most important.

Investigations into multielement techniques of analysis, including emission-spectrographic arc and solution techniques, neutron activation and (although not a multielement technique) atomic-absorption spectrophotometry, have shown that not all elements of interest can be determined by any one technique. Interference and matrix effects, and poor sensitivities for certain elements, e.g., arsenic, selenium, and tellurium by emission spectrography, and of cadmium, nickel, and iron by instrumental neutron-activation analysis, are the main factors that prevent this.

Chemical procedures involving a final spectrophotometric determination of arsenic, germanium, molybdenum, nickel, phosphorus, tellurium, tin, and titanium were therefore considered. For selenium, fluorimetry was used. In general these were adaptations of established procedures, modified to deal with the complex nature of the concentrates to be analysed. These concentrates may have lead contents of up to 70 per cent, zinc contents of up to 55 per cent, and copper contents of up to 30 per cent, with significant amounts of iron and silica.

2. DISSOLUTION PROCEDURES

Two common alternatives for the decomposition of sulphide samples are wet oxidation with bromine, nitric acid, and perchloric acid, or fusion with a mixture of sodium peroxide and sodium carbonate. Precipitation of the insoluble lead sulphate formed by either of these two procedures can then be avoided by the addition of complexing agents such as tartrate, acetate, or ethylenediaminetetra-acetic acid (EDTA), provided that the subsequent steps can be conducted at relatively high pH values (greater than 3), e.g., in the determination of nickel, molybdenum, tin, and titanium. This approach was used for the preparation of solutions for the determination of nickel (acid digestion), molybdenum, tin, and titanium (Na₂O₂-Na₂CO₃ fusion). In the determination of arsenic, tellurium, selenium, and germanium, where the subsequent analytical procedure requires solvent extraction from acids of high molarity (except for selenium at a pH value of 1.1), this approach failed because the lead sulphate remained insoluble in the presence of these complexing agents, and because the sodium chloride introduced in the fusion step crystallized from the solutions. In the determination of arsenic and tellurium, however, this difficulty was overcome by dissolution of the residual lead sulphate in a mixture of hydrobromic and hydrochloric acids. A similar dissolution step could not be used in the determination of selenium and germanium because of possible losses of volatile halides during digestion of the mixed halogen acids. For these determinations, the lead sulphate and sodium chloride (when present) were separated by centrifuging or by filtration. No retention of selenium or germanium was observed in these salts when 2 and 6 \( \mu g \) respectively were recovered from the lead sulphate that had been separated from a sulphide sample having a lead content of 71 per cent.

3. SEPARATION OF INDIVIDUAL ELEMENTS

Liquid-liquid extraction, followed by back extraction and the formation of complexes between the element of interest in the back extract and a suitable chromogenic agent, was used for the determination of germanium, arsenic, molybdenum, and nickel. Selenium was determined directly on the organic extract by fluorimetric measurement. The remaining four elements, phosphorus, tin, titanium, and tellurium, were first separated from the matrix elements and concentrated by coprecipitation, after which the precipitate was dissolved and the individual elements, with or without further separation, were suitably complexed for spectrophotometric measurement (see Table 1).

Although most of these procedures are based on published data, none was directly applicable, and the choice of a suitable combination of steps led to the development of suitable methods. The problems encountered before the final methods were derived, and the proposed solutions, can be summarized as follows.

3.1. Arsenic

The principal problem associated with this determination was the achievement of complete dissolution with acids so that the trivalent halide of arsenic could then be extracted into benzene. This was done by digestion with nitric acid and bromine water for decomposition of most of the sulphides, followed by fuming with perchloric acid and dissolution of the residual salts in a mixture of
TRACE ELEMENTS IN SULPHIDE CONCENTRATES

hydrochloric and hydrobromic acids\textsuperscript{1}. In this way, a complete dissolution of the lead sulphate was obtained. The final acid concentrations from which the extraction takes place are 2.2 M hydrobromic acid and 8.4 M hydrochloric acid. The arsenic is then back-extracted into water and determined by the molybdenum-blue\textsuperscript{1} spectrophotometric procedure.

3.2. Germanium

Chlorine that is generated when the fusion mixture is acidified with hydrochloric acid is extracted into the carbon tetrachloride along with the germanium and prevents complete development of the germanium–phenylfluorone complex. The addition of phenol (as recommended by McGee et al.\textsuperscript{13}) for the removal of free bromine in the determination of selenium was found to be effective in countering interference from chlorine. When the aqueous phase has been adjusted to 9 M hydrochloric acid before the extraction step, sodium chloride is precipitated and removed, together with insoluble lead sulphate, by filtration. A germanium loss of less than 2 per cent was observed when 8 \textmu g of germanium was separated from 0.5 g of lead sulphate and the sodium chloride separated in the procedure.

3.3. Molybdenum

One of the most sensitive spectrophotometric methods for the determination of molybdenum is that involving extraction of its complex with dithiol into petroleum ether\textsuperscript{14}. However, this method is not directly applicable to samples containing more than 1 mg of copper\textsuperscript{7}, and a preliminary separation step is necessary.

The extraction of molybdenum with oxine from an acid medium is highly selective. The last traces of interfering elements can readily be eliminated by washing of the organic extract with 0.1 M oxalic acid\textsuperscript{15}. As the lead sulphate would precipitate from an acid solution of this type of material, the extraction was carried out from a buffered solution of pH value 4 to 5 in the presence of EDTA. A clear solution of a sample can be obtained by fusion with Na\textsubscript{2}CO\textsubscript{3}–Na\textsubscript{2}O\textsubscript{3}, leaching with water, and boiling in the presence of EDTA, followed by the addition of acetic acid to a pH value of 4 to 5. The recovery of the molybdenum added to the solutions derived from a lead sulphide concentrate was 94 per cent at a molybdenum content of 9 \textmu g. For maximum accuracy, a calibration curve should be prepared for standard solutions carried through the entire oxine and subsequent dithiol extractions.

3.4. Nickel

The sample is decomposed with hydrochloric and nitric acids and, after the trivalent and tetravalent ions have been masked with tartaric acid\textsuperscript{16}, the copper with sodium thiosulphate\textsuperscript{17}, and the manganese by reduction with hydroxylamine hydrochloride\textsuperscript{4}, the yellow complex of nickel with dimethylglyoxime is extracted at a pH value of 5.0 to 5.3 into chloroform. The chloroform extract is washed with dilute ammonia for the removal of any copper co-extracted with the nickel. The nickel is back-extracted into 0.5 N hydrochloric acid and the red nickel\textsuperscript{16}–dimethylglyoxime complex is developed in aqueous solution for spectrophotometric measurement. The molar absorptivity of this complex is about four times that of the complex extracted into chloroform.

3.5. Phosphorus

The method used is based on the extraction\textsuperscript{12} of the phosphovanadomolybdate complex from a medium of perchloric and nitric acids into methyl isobutyl ketone (MIBK). Modifications were made to allow for the removal of silica, which can occlude phosphorus, for the use of a direct procedure for the determination of phosphorus down to 100 p.p.m., and for its separation by co-precipitation with the iron\textsuperscript{13,14} from the fusion salts and major constituents of the samples that are not precipitated by ammonium hydroxide. The limit of determination can thus be reduced to 10 p.p.m. of phosphorus in the sample.

3.6. Selenium

The sample was originally decomposed by sintering with Na\textsubscript{2}CO\textsubscript{3}, NaCl, and NaClO\textsubscript{3} in a Pyrex tube. A cleaner dissolution was obtained by oxidation at room temperature with bromine, followed by digestion with nitric and phosphoric acids. The method of determination was that given by Crenshaw and Lakin\textsuperscript{15}.

3.7. Tellurium

After dissolution of the sample with nitric, perchloric, and hydrobromic acids, the tellurium and most of the mercury, antimony, tin, and gold are isolated by a double co-precipitation with arsenic as
the carrier. Before the bromotelluride is extracted with rhodamine 3B into benzene, the mercury, antimony, and tin are removed as volatile bromides, and the gold is removed by filtration after it has been reduced to the metal. When the benzene extract is stripped with a sulphuric acid solution containing only the dye and no bromide, the tellurium, which forms a weak bromide complex, is back-extracted into the aqueous phase, leaving any remaining gold, mercury, platinum, and thallium in the organic extract. From the aqueous phase, the tellurium is re-extracted into benzene in the presence of bromide and it is determined spectrophotometrically.

3.8. Tin

After the addition of EDTA to mask the major constituents (copper, lead, zinc, and iron), the tin was separated from the other constituents by co-precipitation with beryllium as the hydroxide. The tin was then separated from the beryllium by extraction with thenoyltrifluoroacetone (TTA) in methyl isobutyl ketone, followed by back-extraction with 1.2 N sulphuric acid in the absence of chloride ion. Phenylfluorone was used as the chromogenic agent.

3.9. Titanium

Extraction of the thiocyanate complex of titanium by tri-n-octylphosphine oxide dissolved in cyclohexane is a sensitive procedure but cannot be applied in the presence of such large amounts of copper, lead, zinc, and iron as are present in sulphide concentrates, because of precipitation of the thiocyanate complexes of at least iron, copper, and zinc. The titanium was isolated from the elements forming interfering thiocyanate complexes (e.g., niobium, tungsten, molybdenum, tellurium) by co-precipitation from a cold ammoniacal solution with magnesium as a carrier after EDTA had been added to form complexes with the elements that would co-precipitate, e.g., lead, copper, zinc, iron, nickel, vanadium, molybdenum, chromium. The titanium was then complexed with thiocyanate and extracted. The extracted complex obeys Beer's Law up to a titanium concentration of at least 1.7 p.p.m. The recovery of the precipitation step was found to be 99 per cent for a mass of 25 μg of titanium, falling to 75 per cent for a mass ranging from 2 to 10 μg of titanium. The limit of determination could, however, be reduced to 10 p.p.m. by the addition of sufficient standard titanium solution to ensure complete (99 per cent) recovery of all the titanium. Correction would then have to be made for the amount of titanium added.

4. APPLICABILITY OF THE PROCEDURES ADOPTED

The applicability of the procedures with regard to mass of sample, limit of determination, and reproducibility are summarized in Table 2.

Details of the individual procedures are given in Appendixes I to IX. A comparison of the values obtained by these methods and those obtained by other techniques is given in Table 3. The only significant disagreement is for tellurium in the zinc sulphide concentrate.

5. CONCLUSIONS

Satisfactory alternative methods for the determination of nine trace elements in sulphide concentrates were established. These elements are not readily determined, either as a group or individually, by other (chiefly instrumental) techniques. The precision obtained ranges from 2.5 to 5.5 per cent at the low p.p.m. level, and the values determined for three sulphide concentrates compare well with those obtained by alternative methods.

6. REFERENCES


## Table 1

### Summary of procedures

<table>
<thead>
<tr>
<th>Element</th>
<th>Initial separation procedure</th>
<th>Recovery</th>
<th>Chromogenic agent and medium</th>
<th>Extraction medium</th>
<th>Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>Extrn with C(_2)H(_4) from 2 M HBr + 8 M HCl</td>
<td>Back extrn with H(_2)O</td>
<td>NH(_4) molybdate + reduction</td>
<td>Spectrophotometric</td>
<td></td>
</tr>
<tr>
<td>Germanium</td>
<td>Extrn with CCl(_4) in 9 M HCl</td>
<td>Back extrn with H(_2)O</td>
<td>Phenylfluorone from 2.8 per cent H(_2)SO(_4)</td>
<td>Spectrophotometric</td>
<td></td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Extrn of oxine complex into CHCl(_3) at pH 4</td>
<td>Wet oxidn</td>
<td>Dithiol from 6.2 N HCl</td>
<td>Petr. ether</td>
<td>Spectrophotometric</td>
</tr>
<tr>
<td>Nickel</td>
<td>Extrn of DMG complex into CHCl(_3), pH 5.0 to 5.3, in tartaric acid, sodium thiosulphate medium</td>
<td>Back extrn with 0.5 N HCl</td>
<td>DMG</td>
<td>Spectrophotometric</td>
<td></td>
</tr>
<tr>
<td>Phosphorus (a)</td>
<td></td>
<td></td>
<td>NH(_4) vanadomolybdate from HNO(_3)-HClO(_4)</td>
<td>MIBK</td>
<td>Spectrophotometric</td>
</tr>
<tr>
<td>Phosphorus (b)</td>
<td>Co-ptn with Fe at pH 6.5 to 7.0</td>
<td>Wet oxidn</td>
<td>NH(_4) vanadomolybdate from HNO(_3)-HClO(_4)</td>
<td>MIBK</td>
<td>Spectrophotometric</td>
</tr>
<tr>
<td>Selenium</td>
<td></td>
<td></td>
<td>2-3 dianionaphthalene from HNO(_3)-H(_2)PO(_4) (pH 1.1)</td>
<td>Cyclohexane</td>
<td>Fluorimetric</td>
</tr>
<tr>
<td>Tellurium</td>
<td>Co-ptn with As in HCl- HBr mixture</td>
<td>Dissolv in HCl-HNO(_3)</td>
<td>Bromothalluridodrhodamine complex, 8 N H(_2)SO(_4), 2% KBr</td>
<td>Benzene</td>
<td>Spectrophotometric</td>
</tr>
<tr>
<td>Tin</td>
<td>Co-ptn with Be as hydroxide, extrn with TTA in MIBK from 1.2N H(_2)SO(_4) + 2N HCl</td>
<td>Back extrn with 1.2N H(_2)SO(_4),</td>
<td>Phenylfluorone from 1.2N H(_2)SO(_4),</td>
<td>Spectrophotometric</td>
<td></td>
</tr>
<tr>
<td>Titanium</td>
<td>Co-ptn as hydroxide with Mg from ammoniacal medium</td>
<td>Dissolv with HCl</td>
<td>Extrn of NH(_4)CNS complex into cyclohexane + TOPO from 7 M HCl</td>
<td>Spectrophotometric</td>
<td></td>
</tr>
</tbody>
</table>
TABLE 2

Evaluation of procedures adopted

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass g</th>
<th>Limit of determination p.p.m. in sample</th>
<th>Coeff. of variation at p.p.m. level</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Coeff. of variation</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>%</td>
</tr>
<tr>
<td>Arsenic</td>
<td>1.0</td>
<td>2</td>
<td>3.6</td>
</tr>
<tr>
<td>Germanium</td>
<td>0.5</td>
<td>1</td>
<td>2.5</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.5</td>
<td>4</td>
<td>3.0</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.5</td>
<td>4</td>
<td>2.5</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>1.0</td>
<td>10</td>
<td>4.0</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.2</td>
<td>1</td>
<td>4.0</td>
</tr>
<tr>
<td>Tellurium</td>
<td>2.0</td>
<td>0.5</td>
<td>4.0</td>
</tr>
<tr>
<td>Tin</td>
<td>0.5</td>
<td>5</td>
<td>5.4</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.5</td>
<td>10*</td>
<td>3.0</td>
</tr>
</tbody>
</table>

*By use of additions technique
ND = not determined
## TRACE ELEMENTS IN SULPHIDE CONCENTRATES

### TABLE 3
Comparison of results obtained by various methods of analysis

<table>
<thead>
<tr>
<th>Element</th>
<th>Matrix</th>
<th>Proposed methods p.p.m.</th>
<th>Induction-coupled plasma spectroscopy p.p.m.</th>
<th>d.c. arc spectroscopy p.p.m.</th>
<th>Atomic-absorption spectrophotometry p.p.m.</th>
<th>Instrumental neutron-activation analysis p.p.m.</th>
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<tr>
<td>Arsenic</td>
<td>Zinc sulphide</td>
<td>3.5</td>
<td></td>
<td></td>
<td>3.7(a)</td>
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<tr>
<td></td>
<td>Lead sulphide</td>
<td>3.5</td>
<td></td>
<td></td>
<td>4.3(a)</td>
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<tr>
<td></td>
<td>Copper sulphide</td>
<td>3.2</td>
<td></td>
<td></td>
<td>2.8(a)</td>
<td></td>
</tr>
<tr>
<td>Germanium</td>
<td>Zinc sulphide</td>
<td>3.2</td>
<td></td>
<td></td>
<td>&lt; 10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lead sulphide</td>
<td>1.4</td>
<td></td>
<td></td>
<td>&lt; 10</td>
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<tr>
<td></td>
<td>Copper sulphide</td>
<td>1.8</td>
<td></td>
<td></td>
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<tr>
<td>Molybdenum</td>
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<td></td>
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<td>&lt; 10</td>
<td>ND</td>
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<td>Copper sulphide</td>
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<td>Nickel</td>
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<td>-</td>
<td>12</td>
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<td></td>
<td>Copper sulphide</td>
<td>35</td>
<td>30</td>
<td>30</td>
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<tr>
<td>Selenium</td>
<td>Zinc sulphide</td>
<td>0.7</td>
<td></td>
<td></td>
<td>0.5(a)</td>
<td>ND</td>
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<tr>
<td></td>
<td>Lead sulphide</td>
<td>3.6</td>
<td></td>
<td></td>
<td>4.2(a)</td>
<td>&lt; 10</td>
</tr>
<tr>
<td></td>
<td>Copper sulphide</td>
<td>1.3</td>
<td></td>
<td></td>
<td>1.3(a)</td>
<td></td>
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<tr>
<td>Tellurium</td>
<td>Zinc sulphide</td>
<td>0.1</td>
<td></td>
<td></td>
<td>1.6(a) &lt; 10(b)</td>
<td></td>
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<tr>
<td></td>
<td>Lead sulphide</td>
<td>3.4</td>
<td></td>
<td></td>
<td>4.8(a) &lt; 10(b)</td>
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<tr>
<td></td>
<td>Copper sulphide</td>
<td>0.8</td>
<td></td>
<td></td>
<td>0.2(a) &lt; 10(b)</td>
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<tr>
<td>Tin</td>
<td>Zinc sulphide</td>
<td>&lt; 5</td>
<td></td>
<td></td>
<td>&lt; 30</td>
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<tr>
<td></td>
<td>Lead sulphide</td>
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<td>Copper sulphide</td>
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<td>&lt; 10</td>
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<tr>
<td>Titanium</td>
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<td>98</td>
<td>103</td>
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<td></td>
<td>Lead sulphide</td>
<td>52</td>
<td>61</td>
<td>51</td>
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<tr>
<td></td>
<td>Copper sulphide</td>
<td>75</td>
<td>77</td>
<td>60</td>
<td></td>
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</table>

(a) Hydride generation
(b) Three-phase liquid-liquid extraction
ND = not determined

Note: No comparative values available for phosphorus
THE SPECTROPHOTOMETRIC DETERMINATION OF ARSENIC
(Laboratory Method No. 33/9)

This method is an adaptation of the methods described by Gomez Coeda et al. 1 and Shelton. 2

1. REAGENTS
   All the reagents unless otherwise specified are of A.R. grade.
   (1) Nitric Acid
       sp. gr. 1.4.
   (2) Hydrochloric Acid
       sp. gr. 1.19.
   (3) Hydrobromic Acid
       sp. gr. 1.46 to 1.49.
   (4) Perchloric Acid
       sp. gr. 1.67.
   (5) Bromine Water
       Saturate 100 ml of water with bromine by careful shaking.
   (6) Hydrochloric Acid 9 M
       Dilute 150 ml of hydrochloric acid (sp. gr. 1.19) to 200 ml with water.
   (7) Benzene
   (8) Ammonium Hydroxide, 50 per cent (v/v)
       Dilute 50 ml of ammonium hydroxide to 100 ml with water.
   (9) Methyl Orange, 1 g/l
       Dissolve 0.1 g of the reagent in 100 ml of water.
   (10) Potassium Bromate, 0.3 g/l
       Dissolve 0.03 g of potassium bromate in 100 ml of water.
   (11) Ammonium Molybdate, 5 g/l
       Dissolve 0.5 g of (NH₄)₆Mo₇O₂₄·4H₂O in water and dilute to 100 ml.
   (12) Hydrazine Sulphate, 1 g/l
       Dissolve 0.1 g of hydrazine sulphate in water and dilute to 100 ml. Prepare afresh daily.
   (13) Standard Arsenic Solution
       Dissolve 0.1320 g of arsenious oxide in 5 ml of 15 per cent sodium hydroxide solution (consisting of 15 g of sodium hydroxide in 100 ml of water). Add 10 ml of hydrochloric acid and dilute to 500 ml.
       1 ml = 0.2 mg of As.
   (14) Dilute Standard Arsenic Solution
       Dilute 5 ml of the standard arsenic solution (1 ml = 0.2 mg of As) and 75 ml of hydrochloric acid to 200 ml with water.
       1 ml = 5 μg of As.

2. PROCEDURE
   Clean all glassware with a hot 1-to-1 mixture of nitric and sulphuric acids, and wash thoroughly with tap water and then with distilled water. When glassware is used repeatedly for the determination of arsenic, water washes alone are adequate.
   a. Weigh 1.0 g of sample into a 250 ml beaker, add 10 ml of bromine water and 10 ml of nitric acid, cover, and allow to stand till all reaction has ceased.
   b. Add 5 ml of perchloric acid and evaporate to fumes of perchloric acid, reducing the volume to about 2 ml. Cool, add 15 ml of hydrochloric acid, and warm to 40°C to aid dissolution of the salts.
   c. Add 10 ml of hydrobromic acid, allow to stand for 5 minutes, cool, and transfer to a separating funnel, using hydrochloric acid (sp. gr. 1.19) to wash the beaker. Dilute to a final volume of 40 ml with this acid.
   d. Add 30 ml of benzene and shake for 3 minutes. Discard the aqueous phase and wash the benzene by shaking for 30 seconds with 10 ml of 9 M hydrochloric acid. Discard the aqueous phase. Repeat the washing step once.
e. Back-extract the arsenic by shaking the organic phase for 3 minutes with 20 ml of water. Run the aqueous phase into a 50 ml volumetric flask. Wash the benzene with 5 ml of water by shaking for 30 seconds, and add this wash to the flask.

f. Add 1 drop of methyl orange indicator to the aqueous extract and make it just alkaline (yellow) by adding drops of 50 per cent ammonium hydroxide solution. Place the flask in a beaker of boiling water and maintain at this temperature for 20 minutes to expel residual benzene. Remove the flask from the beaker and cool.

g. Just neutralize the solution with 10 per cent hydrochloric acid and add 10 ml in excess. Add 1 ml of potassium bromate (0.3 g/l) and replace the flask in the boiling water. Leave for 5 minutes to oxidize the arsenic and decolorize the methyl orange.

h. Remove the flask from the water, add 5 ml of ammonium molybdate solution (5 g/l), mix and add 1 ml of hydrazine sulphate solution (1 g/l), and mix again. Replace the flask in the boiling water for 10 minutes.

i. Cool to room temperature and dilute to volume and mix. Measure the absorbance at 830 nm in 5 cm cells against that of a blank solution carried through the entire procedure.

3. CALIBRATION
a. Transfer 0, 1, 2, 3, and 4 millilitres of the dilute standard arsenic solution (1 ml = 5 μg of As) to a series of separating funnels. Add 15 ml of hydrochloric acid and 10 ml of hydrobromic acid, mix, and allow to stand for 5 minutes. Make up to a final volume of 40 ml with hydrochloric acid (sp. gr. 1.19).

b. Proceed as described in steps d to i of Section 2.

c. On graph paper, plot a calibration graph of absorbance versus micrograms of arsenic for 5 cm cells at 830 nm.

4. REFERENCES

THE SPECTROPHOTOMETRIC DETERMINATION OF GERMANIUM
(Laboratory Method No. 32/1)

This method is an adaptation of the methods described by Strickland\(^1\), Leong Chee Lu\(^2\), and McGee et al\(^3\).

1. REAGENTS
   All the reagents, unless otherwise specified, are of A.R. grade.
   (1) **Sodium Peroxide**
   (2) **Sodium Carbonate**
       Anhydrous.
   (3) **Hydrochloric Acid**
       sp. gr. 1.19.
   (4) **Hydrochloric Acid, 9 M**
       Dilute 150 ml of the concentrated acid to 200 ml with water.
   (5) **Phenol**
   (6) **Carbon Tetrachloride**
   (7) **Sulphuric Acid, 1 to 1**
       Transfer 50 ml of sulphuric acid (sp. gr. 1.84) into 50 ml of water while constantly stirring.
       Cool to room temperature.
   (8) **Gelatin, 5.0 g/l**
       Dissolve 0.5 g of gelatin (microbiological grade) in 30 ml of water by boiling gently. Cool and dilute to 100 ml.
   (9) **Phenylfluorone, 0.1 g/l**
       Dissolve 0.05 g of Merck's reagent in 75 ml of ethanol and 5 ml of 5 N sulphuric acid by warming gently on a water-bath. Cool and dilute to 100 ml with ethanol. Dilute 20 ml of this solution to 100 ml with ethanol.
   (10) **Standard Germanium Solution**
       Dissolve 0.1000 g of Specpure germanium dioxide in 2.5 g of ammonium oxalate, 2.5 g of oxalic acid, and 100 ml of water by heating gently until all the germanium dioxide has dissolved. Cool and dilute volumetrically to 500 ml.
       1 ml = 0.2 mg of GeO\(_2\).
   (11) **Diluted Germanium Solution**
       Dilute 5 ml of the standard germanium solution to 1 litre.
       1 ml = 1 \(\mu\)g of GeO\(_2\).

2. PROCEDURE
   a. Mix 0.5 g of sample with 2.0 g of sodium peroxide and 0.5 g of sodium carbonate in a vitreous-carbon crucible. Fuse carefully over a low flame until the initial vigorous reaction has subsided. Finally fuse to a tranquil melt.
   b. Leach in 20 ml of water in a 250 ml beaker marked at the 15 ml level. Boil to decompose excess peroxide, and reduce the volume to the 15 ml mark.
   c. Place the beaker in a cold water-bath and just neutralize the solution with hydrochloric acid, keeping the beaker in the water-bath during the neutralization.
   d. Remove the beaker from the water-bath and transfer the solution into a 50 ml volumetric flask using hydrochloric acid (sp. gr. 1.19) as wash solution. Add 0.5 g of phenol (Note) and dilute to volume with hydrochloric acid. Stopper the flask and mix well to dissolve the phenol.
   e. Filter the solution into a 50 ml measuring cylinder through a 12.5 cm no. 541 Whatman filter paper. Transfer 45 ml of the filtrate to a 100 ml separating funnel, using hydrochloric acid (sp. gr. 1.19) to rinse the measuring cylinder into the separating funnel (about 5 ml).
f. Add 20 ml of carbon tetrachloride and shake for 2 minutes. Drain the organic layer into a second separating funnel. Add 10 ml of carbon tetrachloride to the first funnel and again shake for 2 minutes. Transfer this organic extract to the second separating funnel (containing the first organic extract).
g. Add 10 ml of 9 M hydrochloric acid. Shake for 30 seconds and transfer the organic layer to a clean, dry separating funnel. Shake the second separating funnel (containing the 9 M hydrochloric acid) with 5 ml of carbon tetrachloride for 30 seconds and combine this organic layer with that in the clean, dry separating funnel.
h. Add 12 ml of water from a burette and shake for 2 minutes. Discard the organic layer and filter the aqueous layer through a 9 cm no. 41 Whatman filter paper until 10 ml of solution has been collected in a 10 ml measuring cylinder. Transfer 10 ml of the filtrate to a 25 ml volumetric flask, and add 1,4 ml of 1-to-1 sulphuric acid, 1 ml of gelatin, and 5 ml of phenylfluorone, mixing after each addition. Dilute to volume.
i. Mix the solution and allow it to stand for 1½ hours for the colour to develop. Measure the absorbance of the solution at 510 nm in a 5 cm cell against that of the reagents only that had been taken through the procedure from the colour-development stage.

3. CALIBRATION
   a. Transfer 0, 1, 2, 3, and 5 millilitres of the diluted germanium solution (1 ml = 1 µg of GeO₂) to a series of 25 ml volumetric flasks, and dilute to approximately 10 ml with water.
   b. Add 1,4 ml of 1-to-1 sulphuric acid, 1 ml of gelatin, and 5 ml of phenylfluorone, mixing after each addition. Dilute to volume and mix.
   c. Allow to stand for 1½ hours for the colour to develop, and measure the absorbance against that of the reagents only at 510 nm in 5 cm cells.
   d. On graph paper, plot a calibration graph of absorbance versus micrograms of GeO₂.

4. NOTE
   Tests with potassium iodide paper have shown the presence of chlorine in the sample solutions that have been acidified. This chlorine was apparently extracted into the carbon tetrachloride and interfered in the subsequent spectrophotometric procedure. The addition of phenol prior to the extraction step, as used by McGee et al.⁢, proved effective in eliminating this interference.

5. REFERENCES
APPENDIX III

THE SPECTROPHOTOMETRIC DETERMINATION OF MOLYBDENUM
(Laboratory Method no. 42/6)

This method is based on the techniques described by Cook et al.¹ and Stary².

1. APPARATUS
   Special cells having a light path of 1 cm and a width of only 0.4 cm.

2. REAGENTS
   Unless otherwise stated, all the chemicals used are of A.R. grade.

  (1) **EDTA, 0.1 M**
      Dissolve 18.6 g of disodium ethylenediaminetetra-acetate dihydrate in water and dilute to 500 ml.

  (2) **8-Hydroxyquinoline (Oxine), 16 g/l**
      Dissolve 1.6 g of reagent in 95 per cent (v/v) ethanol, and dilute to 100 ml with ethanol.

  (3) **Oxalic Acid, 0.1 M**
      Dissolve 6.3 g of the reagent in water and dilute to 500 ml.

  (4) **Hydrochloric Acid, 6.2 N**
      Dilute 519 ml of hydrochloric acid (sp. gr. 1.19) to 1 litre.

  (5) **Iron Solution**
      Dissolve 5 g of Fe(NH₄)₂(SO₄)₂.12H₂O in 250 ml of 6.2 N hydrochloric acid by gentle heating.

  (6) **Reducing Solution**
      Dissolve 75 g of citric acid and 150 g of ascorbic acid in water and dilute to 1 litre.

  (7) **Potassium Iodide, 500 g/l**
      Dissolve 250 g of potassium iodide in water and dilute to 500 ml.

  (8) **Zinc Dithiol, 3.0 g/l**
      To 0.3 g of reagent in a 100 ml beaker, add 4 ml of ethanol followed by 2 ml of water. Place the beaker on a balance and add 4 g of sodium hydroxide solution (500 g/l). Stir until the dithiol has dissolved. Cool, add 1 ml of thioglycolic acid, and mix until the solution is clear. Transfer to a 100 ml volumetric flask and dilute to not more than 45 ml when the solution will again become cloudy. Add 50 ml of potassium iodide solution (500 g/l), dilute to volume, and mix. Keep in ice and water or in a refrigerator when not in use.

  (9) **Standard Molybdenum Solutions**
      Dissolve 0.0630 g of Na₂MoO₄.2H₂O in 6.2 M hydrochloric acid, and dilute to 250 ml with the same acid.
      1 ml = 100 µg of Mo.
      Dilute 10 ml of this solution to 100 ml with 6.2 M hydrochloric acid.
      1 ml = 10 µg of Mo.
      Dilute 20 ml of this solution to 100 ml with 6.2 M hydrochloric acid.
      1 ml = 2 µg of Mo.
      Dilute 25 ml of this solution to 100 ml with 6.2 M hydrochloric acid.
      1 ml = 0.5 µg of Mo.
      Prepare the diluted solutions before use.

3. DILUTION OF SAMPLE AND AMOUNTS OF REAGENT
   The amounts of samples required and the relevant dilutions are given in Table III-1.

4. PROCEDURE
   a. Mix 0.5000 g of sample in a zirconium crucible with 4 g of Na₂O₂ and 1 g of Na₂CO₃. Fuse over a small flame until the first vigorous reaction has subsided. Increase the temperature until the melt is dull-red, and swirl the crucible until all the material has fused to a clear and tranquil melt. Weigh the same quantities of flux into another crucible, mix, and treat as a sample to give a blank solution for the reagents only.
TRACE ELEMENTS IN SULPHIDE CONCENTRATES

TABLE III-1

<table>
<thead>
<tr>
<th>Estimated amount of Mo p.p.m.</th>
<th>Mass of sample g</th>
<th>Dilution ml</th>
<th>Aliquot portion for extraction ml</th>
<th>Petroleum ether ml</th>
<th>Cell size cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 to 16</td>
<td>0.5</td>
<td>100</td>
<td>25</td>
<td>1</td>
<td>1 Special (see Section 1)</td>
</tr>
<tr>
<td>16 to 100</td>
<td>0.5</td>
<td>100</td>
<td>25</td>
<td>5</td>
<td>1 Normal</td>
</tr>
</tbody>
</table>

b. Place the cold crucible in a 125 ml Pyrex beaker. Add 25 ml of water to the melt and cover with a watch-glass. When the reaction ceases, remove the crucible and wash it thoroughly.

c. Insert a boiling rod and bring the solution to the boil. Continue boiling for 10 minutes. To the hot solution, add 40 ml of 0.1 M EDTA and mix. Acidify slowly with glacial acetic acid to a pH value of 6 to 5. Again bring to the boil and continue boiling until the solution becomes clear (5 to 10 minutes). Cool. Transfer to a 100 ml volumetric flask, dilute to volume, and mix.

d. Transfer a 25 ml aliquot portion to a 100 ml separating funnel. Add 10 ml of glacial acetic acid and mix. Use pH paper to ensure that the pH value is about 4.

e. Add 5 ml of oxine solution and mix. Add 15 ml of chloroform and shake for 2 minutes. Transfer the chloroform layer into a second 100 ml separating funnel. Wash the aqueous phase with 5 ml of chloroform by shaking for 30 seconds.

f. Combine the chloroform extracts. Add 30 ml of 0.1 M oxalic acid solution to the chloroform extract and shake for 30 seconds. Transfer the chloroform layer to a 100 ml beaker. To the aqueous phase in the separating funnel, add 5 ml of chloroform, shake for 30 seconds, and transfer the chloroform phase to the beaker.

g. Evaporate the chloroform to dryness. Add 0,5 ml of sulphuric acid (sp. gr. 1,84) and heat to fumes. Carefully add 3 drops of nitric acid (sp. gr. 1,40) to the fuming sulphuric acid. If the solution is not colourless at this stage, add more nitric acid. Continue fuming for about 10 minutes. Cool. Rinse the walls of the beaker carefully with a small amount of water and again bring to fumes. After fuming for 5 minutes, remove from the hot-plate and cool.

h. Add 1 ml of iron solution to the beaker. Rinse the walls with a small amount (about 5 ml) of 6,2 N hydrochloric acid, and just bring the solution to the boil, swirling it frequently to prevent super-heating.

i. Transfer the solution (it is not necessary to cool it) to a 100 ml separating funnel marked at the 14 ml level, using 6,2 N hydrochloric acid. Rinse the beaker with 4 ml of reducing solution and transfer to the separating funnel. Complete the transfer of the sample solution using 6,2 N hydrochloric acid so that the final volume in the separating funnel is 14 ml. Mix, and allow to stand for 20 minutes.

j. Add 4 ml of potassium iodide solution, and mix. Immediately add 2 ml of zinc dithiol solution and shake thoroughly. Allow the solution to stand for 1 minute. Using a pipette, add the required volume of petroleum ether (see Table III-1). Exactly 2 minutes after mixing with the dithiol solution, shake the funnels by hand for 1½ minutes.

k. Discard the aqueous phase, together with a few drops of the organic phase. Dry the inside of the stem of the funnel with a rolled strip of filter paper. Run the extract directly into the cell. Measure the absorbance of the sample and of the blank solution at 670 nm against petroleum ether. Subtract the absorbance of the blank solution from the absorbance of the sample solution and determine the molybdenum content of the extract from a calibration graph.

5. CALIBRATION

a. Transfer 0 ml, 0.5 ml, 1.5 ml, 3.0 ml, 4.0 ml, and 7.0 ml of diluted standard solution (1 ml = 2 µg of Mo) to 125 ml Pyrex beakers. Reduce the amount of acid by evaporating to a small
volume but not to dryness. Add 15 ml of sodium acetate buffer and 10 ml of 0.1 M EDTA. Bring to the boil and continue boiling for about 5 minutes. Cool.

b. Transfer the solutions to 100 ml separating funnels. Add 10 ml of glacial acetic acid, and mix. Continue as described in steps e to k of Section 4, using 5 ml of petroleum ether for the extraction. Measure the absorbances at 670 nm in 1 cm cells against petroleum ether. Subtract the absorbance of the blank solution from the absorbances of the standard solutions.

c. Repeat the calibration over a range of 0 to 2.5 µg of molybdenum, using 1 ml of petroleum ether and the special cells. Plot calibration graphs of absorbance against micrograms of molybdenum.

6. REFERENCES
APPENDIX IV

THE SPECTROPHOTOMETRIC DETERMINATION OF NICKEL
(Laboratory Method no. 28/9)

This method is based on several previously published techniques.1-5

1. REAGENTS

Unless otherwise stated, all the chemicals used are of A.R. grade.

1. Ammonium Acetate Buffer

Dissolve 50 g of ammonium acetate in about 100 ml of water. Add 2.5 ml of glacial acetic acid and dilute to 250 ml.

2. Hydroxylamine Hydrochloride, 50 g/l

Dissolve 5 g of the reagent in 100 ml of water. Prepare afresh each day.

3. Dimethylglyoxime (DMG), 10 g/l

Dissolve 1 g of dimethylglyoxime, sodium salt (Hopkin & Williams), in 100 ml of water.

4. Ammonium Hydroxide, 2 per cent (v/v)

Dilute 5 ml of ammonium hydroxide (sp. gr. 0.91) to 250 ml.

5. Hydrochloric Acid, 0.5 N

Dilute 42 ml of hydrochloric acid (sp. gr. 1.19) to 1000 ml.

6. Iodine Solution

Dissolve 10 g of potassium iodide in 20 ml of water and add 6.35 g of iodine. Stir until dissolved, and dilute to 500 ml.

7. Sodium Hydroxide Solution, 40 g/l

Dissolve 40 g of the reagent in water, cool, and dilute to 1 litre. Store in a polyethylene bottle.

8. Tartaric Acid, 50 g/l

Dissolve 5 g of tartaric acid in 100 ml of water.

9. Standard Nickel Solution

Dissolve 0.1000 g of nickel sponge in 10 ml of hydrochloric acid (sp. gr. 1.19). Dilute to 100 ml.

1 ml = 1 mg of Ni.

Dilute 5 ml of this solution to 500 ml with 0.5 N hydrochloric acid.

1 ml = 10 μg of Ni.

Dilute 15 ml of this solution to 100 ml with 0.5 N hydrochloric acid.

1 ml = 1.5 μg of Ni.

Prepare both diluted standard solutions afresh daily.

2. DILUTIONS OF SAMPLE AND AMOUNTS OF REAGENT

Table IV-1 lists the dilutions required and the relevant amounts of reagent to be used.

TABLE IV-1

<table>
<thead>
<tr>
<th>Estimated amount of Ni p.p.m.</th>
<th>Mass of sample g</th>
<th>Dilution ml</th>
<th>Aliquot portion for extraction ml</th>
<th>Sodium thiosulphate g</th>
<th>NH₄OH.HCl ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 to 30</td>
<td>0.5</td>
<td>Take all of sample</td>
<td></td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>30 to 50</td>
<td>0.5</td>
<td>50</td>
<td>25</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>50 to 100</td>
<td>0.5</td>
<td>50</td>
<td>15</td>
<td>1.5</td>
<td>1.5</td>
</tr>
</tbody>
</table>
TRACE ELEMENTS IN SULPHIDE CONCENTRATES

3. PROCEDURE
a. To 0.5000 g of sample in a 125 ml Pyrex beaker (tall form), add a few drops of water (to moisten the sample) and 10 ml of hydrochloric acid (sp. gr. 1.19). Mix, and allow to stand at room temperature for 10 minutes. Swirl occasionally. Prepare a blank solution for the reagents only by taking 10 ml of hydrochloric acid (sp. gr. 1.19), and carry it through the entire procedure.

b. Cover the beaker with a watch-glass, bring the solution to the boil, and continue boiling for 10 to 15 minutes. Remove from the hot-plate and add 5 ml of nitric acid (sp. gr. 1.40). After the reaction has ceased, boil for 5 to 10 minutes on the hot-plate. Evaporate to dryness.

c. Rinse the walls of the beaker with water. Add 5 ml of hydrochloric acid (sp. gr. 1.19) and evaporate carefully just to dryness.

d. Add 10 ml of tartaric acid solution, and mix. Add 25 ml of ammonium acetate buffer, insert a boiling rod, cover, and bring the solution to the boil. Continue boiling for 5 minutes. Ignore any small siliceous residue. Cool to room temperature.

e. Add sodium thiosulphate to the solution (see Table IV-1). Stir until dissolved, add hydroxylamine hydrochloride (see Table IV-1), and mix. Transfer to a 100 ml separating funnel. The volume should be between 60 and 70 ml. Add 4 ml of DMG solution and mix.

f. Extract the nickel with three 10 ml portions of chloroform by shaking for 1 minute. Collect the combined chloroform extracts in a second 100 ml separating funnel (Note). Discard the aqueous layer. Wash the chloroform layer with two 20 ml portions of 2 per cent ammonium hydroxide by shaking for 30 seconds. Discard the aqueous layers.

g. Extract the nickel from the chloroform by shaking for 30 seconds with two 5 ml portions of 0.5 N hydrochloric acid. Discard the chloroform layer. Collect the combined acid extracts in a separating funnel and wash with about 2 ml of chloroform. Discard the chloroform layer.

h. Filter the acid extract through a wet 7 cm Whatman no. 541 filter paper into a 25 ml volumetric flask. Rinse the funnel with about 2 ml of water. Stopper and rotate the separating funnel so that the whole interior surface is rinsed. Filter the wash solution, and wash the filter paper with a few millilitres of water. The total volume in the volumetric flask should not exceed 15 ml.

i. Add the following reagents in quick succession to one sample at a time, mixing after each addition:
   1 ml of iodine solution
   2 ml of DMG solution
   5 ml of sodium hydroxide solution
   Dilute to 25 ml and mix.

j. After 30 minutes, measure the absorbance at 470 nm in a 5 cm cell against that of the blank solution. Refer to the calibration graph to evaluate the concentration of nickel in the solution measured.

4. CALIBRATION
Transfer 0, 1, 2, 5, and 10 millilitres of standard nickel solution (1 ml = 1.5 μg of Ni) to 25 ml volumetric flasks. Add 0.5 N hydrochloric acid so that the total amount is 10 ml (i.e., add 10, 9, 8, 5, and 0 millilitres respectively) and proceed as described from step i of Section 3. Construct a calibration graph of absorbance against micrograms of nickel.

5. NOTE
Although the aqueous phase is usually turbid with varying amounts of a blackish precipitate, complete extraction of the nickel is obtained.

6. REFERENCES
TRACE ELEMENTS IN SULPHIDE CONCENTRATES

APPENDIX V

THE SPECTROPHOTOMETRIC DETERMINATION OF PHOSPHORUS
(Laboratory Method no. 15/16)

This method is based on previously published techniques1-3.

1. REAGENTS

Only reagents of low phosphorus content should be used (Note 1). All the reagents, except where otherwise specified, are of A.R. grade.

1. Sodium Peroxide

2. Sodium Carbonate

3. Hydrochloric Acid
   sp. gr. 1.19.

4. Nitric Acid
   sp. gr. 1.42.

5. Nitric Acid, 20 per cent (v/v)
   Dilute 20 ml of nitric acid (sp. gr. 1.42) to 100 ml with water.

6. Ammonia Solution
   sp. gr. 0.91.

7. Ammonia Wash Solution, 2 per cent (v/v)
   Dilute 20 ml of ammonia solution (sp. gr. 0.91) to 1 litre with water.

8. Perchloric Acid
   Merck, sp. gr. 1.67.

9. Iron Solution
   Dissolve 9.66 g of Merck ferric chloride (FeCl₃·6H₂O) in water, and dilute to 100 ml.
   1 ml = 20 mg of Fe.

10. Hydrofluoric Acid, 40 per cent
    Merck.

11. Ammonium Vanadate-Molybdate Solution
    Dissolve 1 g of ammonium vanadate, NH₄VO₃ (Merck), in about 300 ml of water, and then slowly add 140 ml of concentrated nitric acid (sp. gr. 1.42). To this solution, add 40 g of ammonium molybdate [(NH₄)₆Mo₇O₂₄·4H₂O] dissolved in about 400 ml of water. Dilute to 1 litre, and mix well. This reagent must be freshly prepared.

12. Methyl Isobutyl Ketone (MIBK)
    Merck.

13. Standard Phosphorus Solution
    Dissolve in water 0.4393 g of potassium dihydrogen ortho-phosphate (KH₂PO₄, Riedel-de Haen) that has been dried to constant mass at 105°C. Cool, and dilute to 1 litre in a volumetric flask.
    1 ml = 0.1 mg of P.

14. Diluted Standard Phosphorus Solution
    Dilute 100 ml of standard phosphorus solution to 1 litre with water.
    1 ml = 0.01 mg of P.

2. AMOUNT OF SAMPLE

The dilutions for the determination of phosphorus in 1 g samples of sulphide concentrate are given in Table V-1. For values higher than 2000 p.p.m. of phosphorus, suitable variations should be made in mass of sample, amount of aliquot portion, and size of cells.

3. PROCEDURE

3.1. Dissolution of Sample

a. Mix 1 g of sample with 6 g of sodium peroxide in a zirconium crucible, and cover with 0.5 g of sodium carbonate. Mix the same quantities of flux in a zirconium crucible and treat this as a sample to give a blank solution for the reagents only.
TABLE V-1

<table>
<thead>
<tr>
<th>P p.p.m.</th>
<th>Dilution (1) ml</th>
<th>Aliquot portion (1) ml</th>
<th>Dilution (2) ml</th>
<th>Aliquot portion (2) ml</th>
<th>Cell cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 to 100 *</td>
<td>100</td>
<td>100</td>
<td>50</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>100 to 400 †</td>
<td>100</td>
<td>20</td>
<td>50</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>400 to 2000</td>
<td>100</td>
<td>5</td>
<td>50</td>
<td>25</td>
<td>5</td>
</tr>
</tbody>
</table>

* Method using coprecipitation with iron.
† Direct method.

b. Fuse over a Meker burner, using a low flame at first and gradually increasing the temperature until the fusion is complete. Cool the crucible and place in a 400 ml beaker.
c. Add 80 ml of 1-to-1 hydrochloric acid to the beaker, cover with a watch-glass, and heat if necessary to dissolve the salts. Rinse with a minimum of water, and remove the crucible.
d. Transfer the contents of the beaker to a 100 ml volumetric flask, cool to room temperature, and dilute to volume with water.

### 3.2. Direct Method

This method is used for samples containing over 100 p.p.m. of phosphorus.
a. Transfer a 20 ml aliquot portion of the solution resulting from step d of Section 3.1 or a suitable smaller aliquot portion (see Table V-1, Section 2) to a 500 ml beaker, add 20 ml of nitric acid and 20 ml of perchloric acid, cover the beaker, and boil until the first fumes of perchloric acid appear.
b. Remove from the hot-plate, cool, and transfer the contents to a platinum dish, rinsing with a minimum of water. Add 3 ml of hydrofluoric acid to the platinum dish, stir, and place on a heated sand-bath.
c. Evaporate to fumes of perchloric acid, stirring occasionally, and allow to fume strongly for 3 minutes.
d. Remove the platinum dish from the sand-bath, cover, and allow to cool.
e. Transfer the contents by means of a thin-stemmed funnel to a 50 ml volumetric flask, rinsing the platinum dish with hot water. Cool the flask to room temperature, and dilute to the mark.
f. If any salts precipitate out, filter through a Whatman no. 541 filter paper. Take a 25 ml aliquot portion, and proceed with the colour development as described in Section 3.4.

### 3.3. Separation of Phosphorus by Co-precipitation with Iron

This method is used for samples containing between 10 and 100 p.p.m. of phosphorus.
a. Quantitatively transfer the solution (100 ml) resulting from Section 3.1 to a 500 ml beaker.
b. Add 7.5 ml of the iron solution to the beaker, mix, and dilute to approximately 150 ml.
c. Heat just to boiling, remove from hot-plate, and add ammonia solution drop by drop from a dropping-bottle, stirring continuously until the iron is completely precipitated and a pH value of 6 to 7 is obtained as shown on pH paper. Place the beaker on a hot-plate, and allow the precipitate to digest and settle for approximately 15 minutes.
d. Filter hot through a Whatman no. 541 filter paper, and rinse out the beaker with 2 per cent (v/v) ammonia wash solution. A rubber policeman or a small piece of filter paper can be used to remove the iron precipitate adhering to the sides of the beaker. If paper is used, add it to the bulk of the precipitate and wash 2 or 3 times with 2 per cent (v/v) ammonia solution.
e. Allow to drain completely, and place the paper and precipitate in a 500 ml beaker. Add 40 ml of nitric acid and 20 ml of perchloric acid, cover the beaker, and boil to decompose the paper and dissolve the precipitate. Continue heating until the first fumes of perchloric acid appear.
f. Remove from the hot-plate, cool, and transfer the contents to a platinum dish, rinsing the beaker and watch-glass with a minimum of water.
g. Add 3 ml of hydrofluoric acid, stir, and place on a heated sand-bath.
h. Evaporate to fumes of perchloric acid, and allow to fume strongly for 3 minutes.
i. Remove the dish from the sand-bath, cover, and allow to cool.
j. Using a thin-stemmed funnel, transfer the contents of the platinum dish to a 50 ml volumetric flask, and rinse with hot water. Cool to room temperature and dilute to the mark.
k. Take a 25 ml aliquot portion and proceed as described in Section 3.4.

3.4. Development of Colour and Measurement
a. Transfer a 25 ml aliquot portion, obtained as described either in step k of Section 3.3, or step f of Section 3.2, and the corresponding blank solutions to 500 ml beakers. Add 10 ml of water and 5 ml of 20 per cent (v/v) nitric acid and boil for 3 minutes.
b. Remove the beaker from the hot-plate, add 25 ml of ammonium vanadate–molybdate solution from a pipette, mix, and place in a cold water-bath. Cool to 20 °C, and allow to stand for 1 hour (Note 2).
c. Transfer the solution to a 250 ml separating funnel marked at the 80 ml level, rinse, and dilute to this mark with water.
d. Using a pipette, transfer 20 ml of MIBK to the separating funnel, stopper, and shake for 2 minutes.
e. Allow the phases to separate for 5 minutes, and drain off the lower (aqueous) phase.
f. Roll up a quarter segment of filter paper, e.g., Whatman no. 541, and fit it as a plug in the stem of the separating funnel.
g. Place a clean, dry 125 ml beaker under the funnel and run off the organic layer drop by drop into the beaker. Cover the beaker with aluminium foil.
h. Measure the absorbance i n appropriate cells (5 or 1 cm) at 425 nm against that of pure MIBK, making corrections for the absorbance of the blank solutions. Readings should be made within 30 minutes of the extraction.

4. CALIBRATION
Since calibration graphs for the direct and co-precipitation methods are virtually identical, one calibration graph, applicable to the direct method for simplicity, can be applied to both procedures.
a. For calibration with a 5 cm cell, transfer 0 ml, 0.5 ml, 1 ml, 2 ml, 4 ml, and 5 ml of the standard phosphorus solution (1 ml = 10 μg of P) to separate 400 ml beakers. For a calibration with a 1 cm cell, transfer 0, 5, 10, 20, and 25 millilitres of the same solution to separate 400 ml beakers.
b. Add 10 ml of perchloric acid to each of the beakers and 5 ml of 20 per cent (v/v) nitric acid, and dilute to a volume of 40 ml with water (Note 3).
c. Cover the beakers, place on a hot-plate, and boil for 3 minutes.
d. Remove from the hot-plate, and continue as described in steps b to h of Section 3.4.
e. Plot a calibration graph of absorbance against amount of phosphorus in micrograms.

5. NOTES
(1) Most detergents contain phosphorus. All traces of detergents should be removed from the glassware by treatment with a 1-to-l mixture of nitric and sulphuric acids or with hot hydrochloric acid, and thorough rinsing with tap and distilled water.
(2) At a temperature of 20 °C, the colour development is complete after the solution has stood for 7 minutes, but it may be retarded if titanium or zirconium is present. Complete colour development is obtained for samples of up to 2 per cent titanium and 0.5 per cent zirconium by an increase in the standing time to 1 hour.
(3) It is important to maintain the same acidity for sample, blank, and standard solutions. If aliquot portions different from those given in Table V-1 are taken, the requisite amounts of perchloric acid (10 ml) and 20 per cent (v/v) nitric acid (5 ml) must be present in a 40 ml volume solution before the addition of 25 ml of molybdate–vanadate reagent.

6. REFERENCES
THE FLUORIMETRIC DETERMINATION OF SELENIUM
(Laboratory Method no. 34/4)

1. APPARATUS
   (1) Fluorimeter
       A Fluorimeter instrument with an FM 102 lamp having a spectral range of 300 to 400 nm, an
       excitation filter OX 1 (366 nm optimum wavelength), and an emission filter OY 13 (525 nm
       optimum wavelength).
   (2) Centrifuge Tubes
       15 ml capacity.
   (3) Fluorimeter Tubes
       10 mm by 75 mm.
   (4) Erlenmeyer Flasks
       50 ml capacity.

2. REAGENTS
   All the reagents, unless otherwise specified, are of A.R. grade.
   (1) Nitric Acid
       sp. gr. 1.40.
   (2) Phosphoric Acid
       sp. gr. 1.71.
   (3) Hydrochloric Acid
       sp. gr. 1.19.
   (4) Nitric Acid, 4N
       Dilute 255 ml of nitric acid (sp. gr. 1.40) to 1 litre.
   (5) Hydrochloric Acid, 0.1N
       Dilute 8.3 ml of hydrochloric acid (sp. gr. 1.19) to 1 litre.
   (6) Bromine
   (7) Hexane
   (8) Cyclohexane
   (9) Hydroxylamine Hydrochloride
       NH₂OH.HCl.
   (10) Ammonium Oxalate, Saturated Solution
       Dissolve 20 g of ammonium oxalate in 200 ml of boiling water. Allow to cool and decant the
       supernatant liquor.
   (11) Sodium Tartrate, 100 g/l
       Dissolve 10 g of di-sodium tartrate, (CHOH.COONa)₂.2H₂O, in 100 ml of water.
   (12) Complexing Solution
       Dissolve 30 g of the di-sodium salt of EDTA in 1 litre of a 10 per cent solution of
       hydroxylamine hydrochloride in water.
   (13) Ammonium Hydroxide, 4N
       Dilute 300 ml of ammonium hydroxide (sp. gr. 0.91) to 1 litre with water.
   (14) Selenium Solutions
       a. Standard Solution
           Dissolve 0.5 g of pure selenium (99.99 per cent) in 14.5 ml of nitric acid. Add 112 ml of
           nitric acid and dilute to 500 ml.
           1 ml = 1000 µg of Se.
       b. Working Solution
           Prepare a working solution containing 1 µg of selenium per millilitre of solution in 4N
           nitric acid by successive dilutions of the standard solution. In each case, dilute 10 ml of the
           stronger solution to 100 ml with 4N nitric acid.
           1 ml = 1 µg of Se.
(15) **DAN Solution, 1 g/l**
Dissolve 0.5 g of 2,3-diamino-naphthalene (DAN) in 50 ml of hydrochloric acid (sp. gr. 1.19) and dilute to 500 ml with water. Extract three times with 25 ml portions of cyclohexane, discarding the organic phase each time. Extract three times with 25 ml portions of hexane, discarding the organic phase each time. Store the solution, in a dark-coloured bottle under a 0.5 cm layer of hexane, in a refrigerator.

3. **PROCEDURE**
   a. Transfer 0.2 g of sample into a 15 ml centrifuge tube, add 0.5 ml of bromine, and allow to stand for 15 minutes. To a separate centrifuge tube, add 0.5 ml of bromine, and treat in the same way as a sample to give a blank solution for the reagents only.
   b. Add 5 ml of nitric acid (sp. gr. 1.40), place the tube in a hot water-bath, and allow the reaction to proceed gradually until it has ceased. Add 3 ml of phosphoric acid, and leave in the water-bath for 1 hour. Agitate the solution occasionally.
   c. Cool and make up to a volume of 12 ml. Stopper and mix. Remove the stopper and centrifuge for 5 minutes. Using a pipette, transfer 10 ml of the supernatant solution to a 50 ml Erlenmeyer flask. Add 3 ml of water, and heat to boiling to reduce the volume to approximately 8 ml (Note 1).
   d. Cool the solution slightly, add 10 ml of ammonium oxalate solution, and boil for 10 minutes. Cool, add 5 ml of 4N ammonium hydroxide solution, and adjust the pH value to 1.1 (using a pH meter) with 4 N ammonium hydroxide. Add 1 ml of sodium tartrate solution (100 g/l) and 5 ml of complexing solution. The volume should be approximately 40 ml at this stage (Note 2).
   e. Subdued light is required during the subsequent steps of the analysis.
   f. Add 3 ml of DAN solution (1 g/l), heat to about 50°C, and allow to stand in the dark for 1 hour.
   g. Transfer the solution to a separating funnel, washing the flask with a minimum amount of water to a final volume of approximately 45 ml. Add 5 ml of cyclohexane from a pipette and shake for 30 seconds. Allow the phases to separate, and discard the aqueous phase.
   h. Wash the organic phase by shaking twice with 25 ml portions of 0.1 N hydrochloric acid for 5 seconds each time. Discard the aqueous phases.
   i. Transfer the organic phase to a clean centrifuge tube and centrifuge for 2 minutes to ensure that all water is removed. Pour a small amount of the organic phase into a fluorimeter tube, and measure the fluorescence against that of the blank solution.

4. **CALIBRATION**
   a. Transfer 0.5 ml, 1.0 ml, 1.5 ml, 3.0 ml, and 5.0 ml of the selenium solution (1 ml = 1 µg of Se) to a series of 50 ml Erlenmeyer flasks. Conduct a blank solution from this step onwards.
   b. Add 5 ml of nitric acid and 5 ml of phosphoric acid to each flask, and boil until the volume is reduced to approximately 8 ml.
   c. Proceed from step d of Section 3 to step h (the fluorescence measurement).

5. **MEASUREMENT OF FLUORESCENCE**
   a. Set the Fluorimeter instrument at 0 on water. Adjust the scale reading to 100 against the highest standard (Note 3), e.g., 5 µg of Se = 100. Measure the other standards and the samples, including the respective blank solutions on this setting. Subtract the readings for the respective blank solutions.
   b. Construct a calibration graph of micrograms of selenium versus scale reading and determine the amount of selenium in the sample solution.

6. **CALCULATION**
   Calculate the amount of selenium in the samples as follows:

\[
Se, \text{ p.p.m.} = \frac{Se (\mu g) \times 1.2}{\text{Mass of sample (g)}}
\]
7. NOTES

(1) Evaporation to an 8 ml volume also helps to remove excess bromine.

(2) After the addition of ammonium oxalate solution, the determination for an individual sample or a batch of samples must continue without interruption until the extraction of the piazselenol has been completed.

(3) If less than 1 p.p.m. of selenium is to be determined, prepare a more dilute standard selenium solution (1 ml = 0.1 μg of Se) by diluting 10 ml of the standard solution (1 ml = 1 μg of Se) to 100 ml with 4 N nitric acid. Now set the fluorimeter using the highest standard of the diluted solution to 100, e.g., 0.5 μg = 100.

8. REFERENCE

1. REAGENTS
   Unless otherwise stated, all the chemicals used are of A.R. grade.
   (1) Dilute Hydrochloric Acid, 1 to 9
       Dilute 100 ml of hydrochloric acid (sp. gr. 1.19) to 1 litre.
   (2) Mixture of Hydrochloric and Nitric Acids
       Heat 100 ml of hydrochloric acid (sp. gr. 1.19) to boiling point. Immediately before use, add 2.5 ml of nitric acid (sp. gr. 1.40). Prepare afresh before use.
   (3) Arsenic Solution, 1 g/l
       Dissolve 0.26 g of As$_2$O$_3$ in a small amount of water containing one pellet of sodium hydroxide. Transfer with water to a 200 ml volumetric flask and dilute to volume.
   (4) Sodium Hypophosphite, 8 per cent
       Dissolve 80 g of the reagent in 500 ml of water. Add 500 ml of hydrochloric acid (sp. gr. 1.19). Mix.
   (5) Sulphuric Acid, approximately 15 N
       Dilute 100 ml of sulphuric acid (sp. gr. 1.84) to 250 ml with water.
   (6) Rhodamine F3B, 0.5 per cent
       Dissolve 0.50 g of the reagent (product of BASF) in about 50 ml of water (see Note 1). Transfer to a 100 ml volumetric flask and dilute to volume.
   (7) Rhodamine F3B, 0.1 per cent
       Dilute 20 ml of 0.5 per cent solution to 100 ml with water.
   (8) Potassium Bromide, 9 per cent
       Dissolve 9 g of the reagent in water and dilute to 100 ml.
   (9) Standard Tellurium Solution
       Dissolve 0.1000 g of elemental tellurium (99 per cent) in about 10 ml of nitric acid (sp. gr. 1.40) by heating. Dilute to 1 litre with water.

\[ 1 \text{ ml} = 100 \mu\text{g of Te}. \]

\[ 1 \text{ ml} = 1 \mu\text{g of Te}. \]

Prepare afresh before use.

2. AMOUNTS OF SAMPLE
   The amounts of sample required and the relevant dilutions are given in Table VII-1.

**TABLE VII-1**

<table>
<thead>
<tr>
<th>Estimated amount of Te p.p.m.</th>
<th>Mass of sample g</th>
<th>Dilution ml</th>
<th>Aliquot portion ml</th>
<th>H$_2$SO$_4$ (sp.gr. 1.84) to add before extraction ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Up to 2</td>
<td>2</td>
<td>Take all the sample</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>2 to 4</td>
<td>1</td>
<td>Take all the sample</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 to 10</td>
<td>1</td>
<td>10</td>
<td>5</td>
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<td>25</td>
<td>5</td>
<td>3.6</td>
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<td>3.8</td>
</tr>
<tr>
<td>75 to 100</td>
<td>1</td>
<td>100</td>
<td>5</td>
<td>3.8</td>
</tr>
<tr>
<td>100 to 250</td>
<td>1</td>
<td>250</td>
<td>5</td>
<td>3.9</td>
</tr>
</tbody>
</table>
3. PROCEDURE
a. To 30 ml of diluted nitric acid (2 to 1), add the sample (see Section 2) in a 300 ml Pyrex beaker. Cover the beaker. Mix the contents and allow to stand at room temperature for about 30 minutes. Prepare a blank solution in the same manner and carry this through the entire procedure.
b. Warm the contents of the beaker, and, when the reaction ceases, add 5 ml of perchloric acid (sp. gr. 1.67) (see Note 2). Partially cover with a watch-glass and evaporate off the nitric acid, mixing frequently during the evaporation.
c. Bring to fumes of perchloric acid. Orange globules of melted sulphur will appear at this stage. Continue with fuming until all the elemental sulphur has been oxidized (Note 3).
d. Cool, rinse the cover-glass and the walls with water, and again bring to fumes.
e. To the cool residue add 25 ml of water and 25 ml of hydrobromic acid (about 48 per cent). Mix and dissolve the soluble salts. Do not heat. A small siliceous residue may occur at this stage. The lead sulphate is completely dissolved.
f. Add 2 ml of arsenic solution and 100 ml of 8 per cent sodium hypophosphite solution. Insert a boiling rod, cover the beaker, and bring to the boil. Maintain boiling for 10 to 15 minutes. A dark-brown colour will appear. On further boiling, a precipitate of elemental arsenic is formed. Allow to stand at room temperature for 2 hours or overnight.
g. Filter through a Whatman no. 540 12.5 cm filter paper. Wash the beaker and the boiling rod three times with dilute hydrochloric acid. Wash the filter paper thoroughly with the same dilute acid. The total volume of washing solution required is 100 ml.
h. Dissolve the precipitate on the filter paper by adding drop by drop the hot mixture of hydrochloric and nitric acids (reagent (2) of Section 1). Do not use more than 8 ml, which is sufficient to give complete dissolution of the precipitate. Collect the solution in the original beaker. Wash the filter paper four times with water (20 ml).
i. Add 10 ml of hydrobromic acid (about 48 per cent) to the solution and let it stand overnight (Note 4).
j. Repeat the precipitation described in step f but omit the addition of arsenic solution (Note 5). Dissolve the precipitate again as described in step h.
k. To the dissolved precipitate add, with a pipette, exactly 4 ml of sulphuric acid (sp. gr. 1.84). Rinse the boiling rod with water and remove it from the solution.
l. Using a hot-plate of moderate temperature, evaporate to fumes of sulphur trioxide. Remove from the hot-plate as soon as the fumes appear. Prolonged fuming would reduce the concentration of sulphuric acid required for the subsequent extraction. Cool.
m. Rinse the walls with a small amount of water, add 3 ml of hydrobromic acid (about 48 per cent), and again bring to fumes of sulphur trioxide, taking the same precautions as in step l. Rinse the sides of the beaker with a small amount of water, and heat to fumes once more.

Transfer the sample or an aliquot portion (see Table VII–1 in Section 2) to a 100 ml separating funnel marked at the 10 ml level. If the whole sample is taken, dilute to 10 ml with water. Otherwise, add the volume of sulphuric acid (sp. gr. 1.84) specified in Table VII–1, cool to room temperature, and dilute to 10 ml. The final concentration of sulphuric acid required is 4 ml per 10 ml volume, i.e., approximately 15 N.
o. To the funnel add 4 ml of 0.5 per cent rhodamine solution and 4 ml of 9 per cent potassium bromide solution. Mix thoroughly after each addition. Add 50 ml of benzene and shake for 2 minutes to extract the tellurium into the benzene.
p. Allow the phases to separate and discard the whole aqueous phase. Add 10 ml of 15 N sulphuric acid and 4 ml of 0.1 per cent rhodamine solution, and back-extract the tellurium into the aqueous phase by shaking for 30 seconds.
q. Transfer the aqueous phase to a clean separating funnel. Wash the benzene phase with 2 ml of 15 N sulphuric acid by shaking for 10 seconds. Combine the washing liquid with the aqueous phase in the second separating funnel.
r. Wash the aqueous phase with 10 ml of benzene by shaking for 30 seconds. Clean the original funnel by washing with water, and transfer the aqueous phase to this funnel. Repeat the washing with 10 ml of benzene. Return the aqueous phase to the second separating funnel (it is not necessary to rinse this funnel).
s. By pipette add 15 ml of benzene to the aqueous phase, followed by 4 ml of 9 per cent potassium bromide solution. Back-extract the tellurium into the benzene by shaking for 3 minutes. From this stage onwards proceed without delay.

t. Discard the aqueous layer and transfer a portion of the benzene extract to a dry centrifuge tube (10 ml). Centrifuge at about 2000 r/min for 60 to 90 seconds.

u. Immediately measure the absorbance of the extract at 560 nm in a 5 cm cell against benzene. Subtract the absorbance of the blank solution from that of the sample, and determine the tellurium content of the extract from a calibration graph.

4. CALIBRATION
   a. Transfer 0, 1, 3, and 5 millilitres of diluted standard tellurium solution (1 ml = 1 µg of Te) to duplicate sets of 300 ml Pyrex beakers. Add 5 ml of perchloric acid and heat to fumes. Cool. (Note 6.)
   b. Proceed as described in Section 3 from step e.
   c. Plot a calibration graph of absorbance against micrograms of tellurium.

5. NOTES
   (1) Rhodamine F3B is equivalent to rhodamine 3B, an ethyl ester of rhodamine B².
   (2) When a 2 g sample is decomposed, the amount of perchloric acid should be doubled.
   (3) Elemental sulphur occludes considerable amounts of selenium and tellurium¹.
   (4) It was found that, when the second precipitation was carried out immediately after the addition of hydrobromic acid, precipitation took much longer and occurred only after prolonged boiling.
   (5) Tests have shown lead to be one element that interferes seriously, although this is not mentioned by Nazarenko et al.¹. It was found, when 2 mg of arsenic was precipitated in the presence of 710 mg of lead, that 70 µg of lead was co-precipitated in a single precipitation, and 1 µg after a double precipitation.
   (6) For accurate work, the procedure as described should be followed. Where a lower degree of accuracy is acceptable, a calibration involving the extractive-spectrophotometric procedure only is used, but the values obtained would be lower by approximately 10 per cent.

6. REFERENCES
THE SPECTROPHOTOMETRIC DETERMINATION OF TIN
(Laboratory Method no. 50/9)

This method is based on the techniques described by Pribil\(^1\) and Stokeley and Moore\(^2\).

1. **REAGENTS**

   All the reagents, unless otherwise specified, are of A.R. grade.

   (1) **Sodium Peroxide**

   (2) **Sodium Carbonate**

      Anhydrous.

   (3) **Acetic Acid**

      Glacial.

   (4) **Hydrochloric Acid**

      sp. gr. 1.19.

   (5) **Sulphuric Acid, 1 to 1**

      Transfer 50 ml of sulphuric acid (sp. gr. 1.84) into 50 ml of water while constantly stirring.

      Cool to room temperature.

   (6) **Sulphuric Acid, 1,2 N**

      Dilute 32 ml of 1-to-1 sulphuric acid to 500 ml.

   (7) **Sulphuric Acid, 1,2 N–Ammonium Chloride 2 M Solution**

      Dissolve 54 g of ammonium chloride in 400 ml of water. Add 32 ml of 1-to-1 sulphuric acid and dilute to 500 ml.

   (8) **EDTA, 100 g/l**

      By gently warming, dissolve 50 g of ethylenediaminetetra-acetic acid (EDTA) in the form of the disodium salt in 400 ml of water. Dilute to 500 ml.

   (9) **Beryllium Solution**

      Dissolve 1.966 g of beryllium sulphate \((\text{BeSO}_4 \cdot 4\text{H}_2\text{O})\) in 100 ml of water.

      1 ml = 1 mg of Be.

   (10) **Ammonium Hydroxide**

      sp. gr. 0.91.

   (11) **Ammonium Hydroxide, 50 per cent (v/v)**

      Dilute 50 ml of ammonium hydroxide (sp. gr. 0.91) to 100 ml.

   (12) **0,2 M 2-Thenoyltrifluoroacetone (TTA) in MIBK**

      Dissolve 11.0 g of C.P.-grade reagent in 250 ml of isobutyl methyl ketone (MIBK).

   (13) **Ammonium Hydroxide, 2 per cent (v/v)**

      Dilute 2 ml of ammonium hydroxide (sp. gr. 0.91) to 100 ml.

   (14) **Hydrogen Peroxide, 30,0 per cent**

   (15) **Gelatin, 10 g/l**

      Dissolve 0.5 g of gelatin (microbiological grade) in 30 ml of water by boiling gently. Cool and dilute to 50 ml.

   (16) **Phenyli fluorone, 0.1 g/l**

      Dissolve 0.05 g of Merck's reagent in 75 ml of ethanol and 5 ml of 5 N sulphuric acid by warming gently on a water-bath. Cool and dilute to 100 ml with ethanol. Dilute 20 ml of this solution to 100 ml with ethanol.

   (17) **Buffer Solution**

      Dissolve 56 g of sodium acetate trihydrate in 150 ml of water. Add 30 ml of acetic acid and dilute to 250 ml.

   (18) **Standard Tin Solution**

      Dissolve 0.1 g of tin (99.9 per cent granular Baker's analysed reagent) in 100 ml of 50 per cent (v/v) hydrochloric acid by warming gently to aid dissolution. Cool. Transfer to a 500 ml volumetric flask. Dilute to volume, and mix.

1 ml = 0.2 mg of Sn.
TRACE ELEMENTS IN SULPHIDE CONCENTRATES

(19) **Diluted Standard Tin Solution**

Using a pipette, transfer 5 ml of standard tin solution to a 200 ml volumetric flask. Add 40 ml of 50 per cent (v/v) hydrochloric acid and dilute to volume with water.

1 ml = 5 μg of Sn.

2. **PROCEDURE**

a. Mix 0,5 g of sample with 2,0 g of sodium peroxide and 0,5 g of sodium carbonate in a vitreous-carbon crucible. Fuse carefully over a low flame until the initial vigorous reaction has subsided. Finally fuse to a tranquil melt. In a separate crucible, fuse the same quantities of flux, and treat as a sample to give a blank solution for the reagents only.

b. Leach in 50 ml of water, and boil to expel excess peroxide. Remove the crucible and wash with water. Add 25 ml of EDTA solution (100 g/l), sufficient acetic acid to make the solution acid (5 to 6 ml is usually sufficient), and boil gently to dissolve all the sample.

c. Dilute the solution to approximately 130 ml. Add 10 ml of beryllium solution (10 mg of Be), heat to between 70 and 80°C, and neutralize with 50 per cent (v/v) ammonium hydroxide, using litmus paper as indicator. Add an additional 10 ml of concentrated ammonium hydroxide and boil for 1 to 2 minutes.

d. Cool in a cold water-bath, filter through a no. 45 12.5 cm Whatman filter paper, and wash 2 or 3 times with water. Add 25 ml of EDTA solution (100 g/l), sufficient acetic acid to make the solution acid (5 to 6 ml is usually sufficient), and boil gently to dissolve all the sample.

e. Add 50 ml of TTA solution, shake for 3 minutes, and allow the phases to separate. Discard the aqueous layer.

f. Shake the organic phase with 10 ml of ammonium chloride-sulphuric acid solution for 30 seconds and discard the aqueous layer. Add 50 ml of the ammonium chloride-sulphuric acid solution plus 0,5 ml of ethyl alcohol, and again shake for 1 minute. Discard the aqueous phase.

g. Back-extract the tin by shaking the organic layer for 15 minutes with 40 ml of 1,2 N sulphuric acid. Drain the aqueous phase into a 100 ml volumetric flask. Add a further 25 ml of 1,2 N sulphuric acid, and shake for 15 minutes. Combine the aqueous extracts.

h. To this 100 ml volumetric flask, add 2,2 ml of 1-to-1 sulphuric acid, 20 ml of buffer solution, 5 to 7 drops of ethyl alcohol, 2 ml of gelatin, and 10 ml of phenylfluorone solution, mixing after each addition. Dilute to volume. Mix and allow to stand for 30 minutes for the colour to develop.

i. Measure the absorbance at 510 nm in 5 cm cells against the blank solution (see Note 2).

3. **CALIBRATION**

a. Transfer 0,1,2,3, and 4 millilitres of the diluted tin solution (1 ml = 5 μg of Sn) to a series of separating funnels. Add 8 ml of hydrochloric acid and 3,2 ml of 1-to-1 sulphuric acid. Dilute to 50 ml with water and mix.

b. Proceed as described in Section 2 e onwards.

c. On graph paper, plot a calibration curve of micrograms of tin versus absorbance for 5 cm cells at 510 nm.

4. **NOTES**

(1) Keep the volume of this solution small enough for it to be transferred to a separating funnel without exceeding a volume of 50 ml.

(2) Measurement of the developed colours should be made within about 5 minutes of the time allowed for colour development.

5. **REFERENCES**


This method is based on the techniques of Pickering and Young and White.

1. REAGENTS

All the reagents, except where otherwise specified, are of A.R. grade.

(1) Sodium Peroxide

(2) Sodium Carbonate

(3) Hydrochloric Acid
Merck, sp. gr. 1.19.

(4) EDTA, 100 g/l
Dissolve 50 g of disodium ethylenediaminetetra-acetate (EDTA) in the dihydrate powder form in hot distilled water, cool, and dilute to 500 ml.

(5) Ammonium Chloride

(6) Ammonia Solution
Merck, sp. gr. 0.91.

(7) Ammonia Wash Solution, 2 per cent (v/v)
Dilute 10 ml of concentrated ammonia to 500 ml with distilled water.

(8) Magnesium Sulphate, 100 g/l
Dissolve 20 g of MgSO₄·7H₂O crystals in hot distilled water, cool, and dilute to 200 ml.

(9) Ammonium Thiocyanate
Merck.

(10) Thioglycollic Acid
Riedel de Haan, C.P. grade.

(11) Cyclohexane
Merck, sp. gr. 0.78.

(12) Tri-n-octylyphosphine Oxide (TOPO), 0.01 M in Cyclohexane
Dissolve 0.39 g of TOPO (Eastman Kodak Co.) in cyclohexane, and dilute to 100 ml with cyclohexane. Keep well stoppered.

(13) Standard Titanium Solution
Grind titanium metal 'sponge' (Johnson Matthey, Speccure grade) in an agate mortar. Transfer 0.0500 g of the pulverized metal to a beaker. Add 60 ml of 1-to-1 (v/v) hydrochloric acid and 5 drops of hydrogen peroxide (30 per cent). Cover, and place on a boiling water-bath until all the metal dissolves (about 5 hours). Cool, and dilute to 100 ml with water.

1 ml = 500 μg of Ti.

(14) Diluted Standard Titanium Solution
Transfer 2 ml of the standard titanium solution to a 100 ml volumetric flask. Add 5 ml of hydrochloric acid, and dilute to the mark with distilled water.

1 ml = 10 μg of Ti.

(15) Titanium Working Solution
Transfer 10 ml of the diluted standard titanium solution to a 100 ml volumetric flask. Add 5 ml of hydrochloric acid, and dilute to the mark with distilled water.

1 ml = 1 µg of Ti.

2. AMOUNT OF SAMPLE

The amount of sample required and the relevant dilutions are given in Table IX-1.

3. PROCEDURE

3.1. Dissolution and Precipitation

a. Transfer 0.5 g of sample (accurately weighed) to a zirconium crucible. Mix with 3 g of sodium peroxide, and cover with 0.5 g of sodium carbonate. Mix the same quantities of flux in a zirconium crucible, and treat this as a sample to give a blank solution for the reagents only.
TABLE IX-1

<table>
<thead>
<tr>
<th>Estimated Ti content p.p.m.</th>
<th>Mass of sample g</th>
<th>Dilution vol. ml</th>
<th>Aliquot portion ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 to 200</td>
<td>0.5</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>10 to 50*</td>
<td>0.5 to 0.6</td>
<td>100</td>
<td>10</td>
</tr>
</tbody>
</table>

*To be checked against a spiked sample for percentage recovery (Note 1).

b. Fuse, gently at first and then to a red heat, on a Meker burner until a clear melt results. Cool.
c. Place the crucible in a 250 ml beaker and leach the melt with a mixture consisting of 20 ml of hydrochloric acid and 25 ml of water. Cover the beaker, and heat to about 60 °C to obtain a clear solution. Rinse the crucible with a minimum of water, and stir the solution. The volume at this stage should be about 50 ml (Note 1).
d. Add 35 ml of EDTA (100 g/l) to the hot solution, and mix.
e. Add 1 g of ammonium chloride to the solution, and mix.
f. Add a piece of red litmus paper to the solution, and from a dropping bottle add concentrated ammonia solution while stirring till the paper just turns blue. Add 5 ml of concentrated ammonia in excess, and stir.
g. Place the beaker in a basin of ice water for approximately 30 minutes until the solution is thoroughly cold.
h. Add 15 ml of magnesium sulphate (100 g/l) and stir briskly for several minutes. Replace the beaker in cold water, and stir briskly at regular intervals until the first signs of precipitate formation (depending on type of sample, between 15 minutes and 1 hour).
i. Continue stirring until a fairly bulky precipitate has formed, and allow to stand overnight.
j. Filter off the precipitate through a Whatman no. 541 filter paper, and wash two or three times with 2 per cent ammonia wash solution.
k. Open the filter paper carefully, and wash the precipitate into the original beaker with a jet of hot water. Add 10 drops of hot concentrated hydrochloric acid to the filter paper to dissolve the remainder of the precipitate, and rinse with 20 ml of hot 1-to-1 hydrochloric acid and then with hot water. Stir to dissolve the precipitate in the beaker. Cool the solution, transfer it to a 100 ml volumetric flask, and dilute to volume with distilled water.

3.2. Extraction and Colour Development

a. Transfer a 5 ml aliquot portion to a 100 ml separating funnel. Add 15 ml of hydrochloric acid (sp. gr. 1.19) (Note 2) and 0.2 ml of thioglycollic acid, and dilute to 25 ml (± 2 ml) with distilled water. Mix and cool under running water to room temperature (Note 3).
b. Add approximately 3.75 g of solid ammonium thiocyanate (top-loading balance is satisfactory) through a short-stemmed, wide-necked funnel, stopper the separating funnel, and shake the funnel well until the solid has dissolved (Note 4).
c. Add 5 ml of the TOPO solution from an A-grade pipette, stopper the separating funnel immediately, and shake in a mechanical shaker for 5 minutes. Allow to stand for approximately 5 minutes, and discard the aqueous layer (Note 5).
d. Roll up a quarter segment of Whatman filter paper (e.g., no. 541) and fit into the stem of the separating funnel as a plug. Run out the organic layer drop by drop into a clean, dry 125 ml Phillips beaker, and cover with aluminium foil.
e. Within 30 minutes, measure the absorbance at a wavelength of 432 nm, using a 1 cm cell, against that of the blank solution, and read the titanium concentration from a calibration graph.
f. Rinse all the glassware with alcohol and water as soon as possible after use to prevent staining by TOPO and thiocyanate complexes.
4. CALIBRATION
Transfer aliquot portions of standard titanium solution (1 ml = 1 \( \mu g \) of Ti) that contain 0, 1, 2, 3, 5, and 6 micrograms of titanium to 100 ml separating funnels. Add 15 ml of hydrochloric acid (sp. gr. 1.19), and take through steps a to e of Section 3.2. Plot absorbance versus concentration of titanium to obtain a calibration curve.

5. NOTES
(1) For samples containing 10 to 50 p.p.m. of titanium, add 2.5 ml of standard titanium solution (1 ml = 10 \( \mu g \) of Ti) to the clear solution obtained from step c of Section 3.1. Use an A-grade 10 ml burette to do this. Stir, and proceed as described in steps d to k of Section 3.1.

\[
T_i = \frac{AD - B}{M} \text{ p.p.m.,}
\]

where

\( A \) = Mass of Ti determined (\( \mu g \)) (step e of Section 3.1)

\( B \) = Mass of Ti added as spike (\( \mu g \))

\( M \) = Mass of sample (g)

\( D \) = Dilution factor

\[
= \frac{\text{Final dilution of sample solution (ml)}}{\text{Aliquot portion taken for extraction (ml)}}
\]

(2) 14.6 ml of 12 M hydrochloric acid (sp. gr. 1.19) is required in a 25 ml volume to give 7 M hydrochloric acid, the optimum acid molarity for extraction. Adjust accordingly for hydrochloric acid of different concentrations.

(3) Cooling is essential because thiocyanate decomposes rapidly in warm solution.

(4) A short-stemmed (about 2.5 cm), wide-necked (about 1.5 cm) funnel is suitable for transfer of the thiocyanate to the separating funnel. If the thiocyanate is difficult to dissolve, rinse the stopper with a few drops of water and shake well. The steps from the addition of thiocyanate to the transfer of the organic phase to the beaker should be carried out with a minimum of delay because of the tendency of the thiocyanate to decompose.

(5) In a highly acidic aqueous phase, ammonium thiocyanate slowly decomposes to form, among other products, polymerized thiocyanic acids and hydrogen cyanide. The aqueous phase from the extraction of the titanium complex should be discarded directly after it has been run off from the organic layer. If this is not feasible, the extracted aqueous phase should be placed in a suitable fume cupboard.

6. REFERENCES