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# Atomic Absorption Methods for Analysis of Some Elements in Ores and Concentrates

by  
Lynn A. Brandvold

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New Mexico Bureau of Mines & Mineral Resources

A DIVISION OF  
NEW MEXICO INSTITUTE OF MINING & TECHNOLOGY



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## *CONTENTS*

### PRELIMINARY CONSIDERATIONS 5

### GENERAL METHODS 7

General Procedure for Acid Decomposition 7

Barium 7

Beryllium 8

Cobalt 9

Copper 9

Iron 10

Lead 10

Nickel 11

Tellurium 11

Zinc 12

### SPECIAL METHODS 14

Acid Pressure Decomposition Technique for Silicate Analysis 14

Analysis of Fluorite for Calcium Carbonate and Calcium Fluorite 15

Copper Oxide in Ores and Concentrates 16

Lead and Zinc in High Grade Ores 16

Manganese in Manganese Ores 17

Mercury in Ores and Concentrates 17

Molybdenum in Molybdenite 18

Molybdenum Oxide in Ores and Concentrates 19

Silver in Ores and Concentrates 19

Tin in Ores and Concentrates 20

### REFERENCES 22

## *PREFACE*

Published methods for rock and ore analysis by atomic absorption are fairly extensive, but scattered. This publication is a compilation of some general and specific procedures for application of atomic absorption analysis to rocks and minerals. In this application, the difficulties and problems lie primarily in the dissolution of the sample. Once dissolution has been effected, the actual atomic absorption analysis is usually relatively simple and straightforward.

This publication, while not a treatise of atomic absorption theory or technique, provides a collection of dissolution methods for analysis of rocks and minerals with major emphasis on ore and concentrate analysis. No attempt has been made to include all elements that can be analyzed by atomic absorption, but only those elements and/or situations for which atomic absorption is the method of choice in our laboratory.

The methods described have been tested and are used by the analytical laboratory at the New Mexico Bureau of Mines & Mineral Resources. The procedures were tested using a double beam atomic absorption unit, the Perkin-Elmer Model 303, equipped with a corrosion-resistant nebulizer. The ranges of liquid standards, detection limits, precision, and occasionally, interferences, depend to some extent on the instrument and the source lamp used in the determinations. Each user will have to test the procedures and determine these parameters for his equipment. Fuel conditions, ranges of liquid standards, detection limits, and precision data in this publication serve only as guidelines. The fuel conditions should be considered as those at ignition, and should be adjusted to optimum on the operator's instrument, using a standard solution. The fuel conditions may also vary with the amount of fuel in the tank. Burner height should also be adjusted to optimum, unless otherwise stated.

Many of these methods have been adapted from referenced papers. Some changes have been made in the methods and the referenced authors should not be held responsible for any inaccuracies which may have been introduced. References are listed twice: at the end of each section, as well as in the general list at the rear of book. Unnumbered references listed at the end of a method pertain to the general method.

The author was privileged to have had informal training in methods of rock and mineral analysis under Dr. Dexter H. Reynolds, former Research Chemist for the Bureau, now retired. Thanks are also due to Dr. Jacques Renault and David Schwab for their critical reading and suggestions.

Socorro  
June, 1974

Lynn A. Brandvold  
Chemist  
New Mexico Bureau of  
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## PRELIMINARY CONSIDERATIONS

All samples should be crushed, coned, and quartered, ground to -100 mesh (except those samples for silver analysis), dried at 110°C for 3 hours, and remixed just before weighing. All solid reagents used for standard solutions should be analytical grade, oven-dried at 110°C for 3 hours, and cooled in a desiccator before weighing. All acids referred to in the text, unless otherwise stated, are analytical grade, concentrated, commercial acids.

There is no general rule or method for the decomposition of a sample for subsequent atomic absorption analysis, because of the nature of the sample and those elements to be analyzed. Methods of decomposition fall into two main classifications: acid, oxidizing and non-oxidizing; and fusion, acid or alkaline flux. The introduction of large quantities of materials to the sample solution should be avoided, because they can cause problems with subsequent atomic absorption analysis: aspirator clog-up, extremely unsteady readings, unstable high background readings, or molecular absorption phenomena. Thus, acid decomposition has an advantage over the use of a flux because the excess acid can be removed. However, acids will not decompose some minerals, and during the course of decomposition will volatilize some elements. A table at the end of this section suggests dissolution methods for some common minerals containing the elements listed in the General Methods section. The analyst should remember these methods are for the pure minerals. When these minerals are encountered in combination with others, the methods may or may not be successful. For an unknown sample, acid decomposition should be the first choice. Fusion is employed if acids will not successfully decompose the sample, or if an element is sought which might be acid volatilized.

When working with perchloric acid several precautions should be observed. *Never allow hot concentrated perchloric acid to contact organic matter.* If an unknown sample is to be heated with perchloric acid, add an amount of nitric acid equal to that of perchloric acid before heating the sample. If a hot solution containing perchloric acid should suddenly turn black, remove the solution from the heat carefully and vacate the area. When the sample is cool, nitric acid can be added and the solution returned to the hotplate. Perchloric acid should never be used in a wooden hood, or in a hood where perchlorates could deposit and

build up. *Hydrofluoric acid can cause severe burns, and plastic gloves should be worn when handling this acid.*

One very promising method for silicate analysis has been proposed by Bernas (1). This method involves using a Teflon-lined steel bomb and the use of a fluoboric-boric acid medium. Silica is not lost under these conditions. This medium provides a salt-free matrix which eliminates many problems in atomic absorption analysis, including the need for releasing, compensating, or complexing agents.

An unknown sample should never be heated in platinum. The presence of elements such as lead, antimony, or arsenic—particularly if there are reducing substances present—can ruin a platinum crucible. Digest an unknown sample first with acid; filter, and wash the filter paper with dilute acid. Place the residue and filter paper in the platinum crucible, burn off the filter paper at low temperature, cool, and mix the residue with flux and fuse. Add the cooled fusion mass to the filtrate from acid digestion, adding more acid if necessary to dissolve the fusion mass; then follow the regular procedure.

The literature contains many conflicting reports of interferences. Marks and Welcher (2) have demonstrated that the magnitude, and in some cases, the direction of interferences depends on a variety of experimental variables, probably accounting for the many discrepancies in the literature. These authors state that interferences can be held at a minimum or eliminated by proper selection of flame conditions and salt conditions. However, large amounts of extraneous ions known to be present in solution should always be checked for possible interferences.

### References

1. Bernas, Bedrich, 1968, A new method for decomposition and comprehensive analysis of silicates by atomic absorption spectrometry: *Anal. Chemistry* v, 40, no. 11, p. 1682-1686.
2. Marks, J. Y., and Welcher, G. G., 1970, Interelement interferences in atomic absorption analyses with the nitrous oxide-acetylene flame: *Anal. Chemistry* v. 42, no. 9, p. 1033-1040.

*Sample dissolution methods*

Element	Sample Type								
	Carbonate	Oxide	Sulfide	Sulfate	Silicate	Arsenide	Arsenate	Aluminate	Native Element
Barium	HCl			Na <sub>2</sub> CO <sub>3</sub> fusion					
Beryllium		Na <sub>2</sub> CO <sub>3</sub> fusion			Na <sub>2</sub> CO <sub>3</sub> fusion			KHSO <sub>4</sub> fusion	
Cobalt			HNO <sub>3</sub> - HClO <sub>4</sub>		acid pressure	HNO <sub>3</sub> - HClO <sub>4</sub>	HCl		
Copper	HNO <sub>3</sub>	HNO <sub>3</sub>	HCl-HNO <sub>3</sub> HClO <sub>4</sub>	H <sub>2</sub> O	HNO <sub>3</sub> - HClO <sub>4</sub>				HNO <sub>3</sub>
Iron	HCl	HCl- H <sub>2</sub> O <sub>2</sub>	HCl-HNO <sub>3</sub> HClO <sub>4</sub>		acid pressure	HNO <sub>3</sub>			HCl
Lead	HCl	HNO <sub>3</sub>	HCl-HNO <sub>3</sub> HClO <sub>4</sub>	15% NH <sub>4</sub> C <sub>2</sub> H <sub>3</sub> O <sub>2</sub>			HNO <sub>3</sub>		
Nickel		HCl	HNO <sub>3</sub>		acid pressure	HCl- HNO <sub>3</sub>	HCl- HNO <sub>3</sub>		
Tellurium		H <sub>2</sub> SO <sub>4</sub>							H <sub>2</sub> SO <sub>4</sub>
Zinc	HCl	HCl- HNO <sub>3</sub>	HCl- HNO <sub>3</sub>		acid pressure				

HCl: hydrochloric acid

HNO<sub>3</sub>: nitric acidHClO<sub>4</sub>: perchloric acidH<sub>2</sub>O<sub>2</sub>: hydrogen peroxideacid pressure: HCl·HNO<sub>3</sub>·HF pressure decomposition—see Special Methods sectionH<sub>2</sub>SO<sub>4</sub>: sulfuric acidNa<sub>2</sub>CO<sub>3</sub>: sodium carbonateKHSO<sub>4</sub>: potassium hydrogen sulfateNH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>: ammonium acetate

## GENERAL METHODS

### GENERAL PROCEDURE FOR ACID DECOMPOSITION

The preferred acid decomposition mixture in our laboratory is a perchloric-nitric-hydrofluoric acid mixture. Perchloric acid is a powerful oxidizing agent whose salts are all water soluble with the exception of potassium, rubidium and cesium. Because perchloric acid is such a powerful oxidizer, nitric acid is employed partly as a diluent, but primarily as a preliminary oxidizer. The hydrofluoric acid

is used to facilitate the decomposition of small amounts of silicates. Silica is partially volatilized and cannot be determined. This acid treatment decomposes most mixtures of oxide and sulfide minerals, and some silicates. Some minerals (magnetite) might require repeated treatment with perchloric acid, as determined by inspecting the residue.

#### Reagents

Hydrochloric acid, 36% (w/w)  
Hydrofluoric acid, 48% (w/w)  
Nitric acid, 70% (w/w)  
Perchloric acid, 72% (w/w)

#### Procedure

1. Weigh the sample into a 400-ml beaker.
2. Add 15 ml of nitric acid, 10 ml of perchloric acid, and 2 ml of hydrofluoric acid; cover with a watch-glass and reflux for about an hour on a hotplate.
3. Remove the cover and evaporate almost to dryness. Cool, and inspect the residue. If any particles remain that appear to be unreacted, add another 10 ml of perchloric acid and evaporate almost to dryness.
4. Add 25 ml of distilled water and heat the solution to boiling. Boil the solution for about 3 minutes. (Alternately, if a chloride system is preferable, add 10 ml of hydrochloric acid, 20 ml of distilled water and bring to a boil. Boil for 3 minutes. Nitric acid may also be used.)
5. Cool. Dilute to 100-ml volume and allow the solids to settle, or filter if desired.
6. Determine the element or elements of interest by atomic absorption, making sure samples and standards contain the same amount of hydrochloric acid or nitric acid if either were used.

### BARIUM

Barium occurs in nature, generally as the sulfate or the carbonate. The sulfate is acid insoluble (with the exception of concentrated sulfuric acid), so a carbonate fusion is usually employed in a barium determination.

Atomic absorption is useful in determining barium, particularly for small amounts of barium where a gravimetric method loses accuracy—especially when calcium and/or strontium are present—since neither of these elements will interfere if a nitrous oxide-acetylene flame is

used. They can interfere in a gravimetric method if they are not previously separated.

Sodium is added to suppress the ionization of barium in the nitrous oxide-acetylene flame. Use of this flame not only reduces chemical interferences, but also greatly increases the sensitivity. High relative amounts of aluminum are reported to interfere with the barium determination, even under the above mentioned conditions (3). However, the authors reported that the interference could be overcome by the addition of 0.15 M ammonium chloride solution. This modification is not included in the procedure given below, but should be utilized if large amounts of aluminum are expected.

#### Reagents

*Barium standard solution*, 1,000 ppm: Dissolve 1.779 g of barium chloride ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ) in distilled water and dilute to one liter with distilled water.

25% *Sodium chloride solution* (w/v): Dissolve 250 g of sodium chloride ( $\text{NaCl}$ ) in 750 ml of distilled water.

0.2% *Sodium carbonate solution* (w/v): Dissolve 2 g of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in distilled water and dilute to one liter with distilled water.

10% *Hydrochloric acid solution* (v/v): Dilute 100 ml of concentrated hydrochloric acid to one liter with distilled water.

*Sodium carbonate*, anhydrous, granular ( $\text{Na}_2\text{CO}_3$ ).

#### Procedure

1. Use a 100- to 500-mg sample if the barium content is expected to be 1% or greater. If the barium content is expected to be less than 1% use a 1.000-g sample.
2. Mix the sample thoroughly with 5 to 7 g of sodium carbonate, place the mixture in a platinum crucible, and cover with a platinum lid. (Barite frequently occurs with sulfides, particularly galena ( $\text{PbS}$ ).  $\text{PbS}$  should be removed first with acids. See Preliminary Considerations, paragraph 5.)
3. Fuse over an open flame until the melt is clear. Pour the melt onto the platinum lid for cooling.
4. Let the melt cool for about 3 minutes, then place the crucible and lid in a 600-ml beaker and slowly add about 100 ml of distilled water. Warm gently until the melt has disintegrated.
5. Filter the solution through Whatman #5 filter paper and discard the filtrate. Wash the residue several times with the 0.2% sodium carbonate solution.
6. Discard the washings, replace the beaker under the funnel with a 100-ml volumetric flask, and dissolve the residue on the filter paper with 20 ml of warm 10% hydrochloric acid. To avoid a violent reaction,



add several ml of distilled water to the filter paper first.

7. Add 2 ml of the sodium chloride solution and dilute to volume with distilled water.
8. Determine barium by atomic absorption at 5536 X using a reducing nitrous oxide-acetylene flame. Add 2 ml of the sodium chloride solution per 100 ml to the standards and blank, and to any sample which has to be diluted. Standards should range from 5- to 50-ppm barium. If samples read lower than 5 ppm, use the expanded scale and make up standards in the range of 0.1 to 1 ppm, or 0.5 to 5 ppm, depending on the samples and which expanded scale is used.

#### Fuel Conditions

Nitrous oxide: 30 psi; flowmeter, 5.5; 11.7 liters/minute.

Acetylene: 10 psi; flowmeter, 13.0; 7.0 liters/minute.

#### Remarks

*Application*—This procedure applies to the determination of barium in most minerals. If there are no sulfates present in a sample, an acid dissolution may be performed, or the same procedure as beryllium may be followed and both barium and beryllium determined on the same solution. In this laboratory we use atomic absorption for determining barium from trace amounts to about 15%. We have been unable to obtain precise results for barium beyond 15%, perhaps because of a combination of instrument noise and large dilution factors. The reasons for the inaccuracy have not been investigated.

*Detection Limits*—The detection limit is about 0.0005% barium when using a 1-g sample and a 10X expanded scale.

*Precision*—A relative deviation of  $\pm 3$  to 5% may be expected; however, for trace analysis a relative deviation of  $\pm 10\%$  may be

expected. References

3. Maruta, T., Takeuchi, T., and Suzuki, M., 1972, Atomic absorption and emission interferences on barium: *Anal. Chim. Acta.*, v. 58, p. 452-455.
- Amos, M. D., and Willis, J. B., 1966, Use of high temperature premixed flames in atomic absorption spectroscopy: *Spectrochim. Acta*, v. 22, p. 1325.
- Bowman, J. A., and Willis, J. B., 1967, Some applications of the nitrous oxide-acetylene flame in chemical analysis by atomic absorption spectrometry: *Anal. Chemistry*, V. 39, no. 11, p. 1210.

### BERYLLIUM

Beryllium occurs in nature chiefly as the oxide or silicate, and less commonly as the silicate-sulfide, the phosphate, or the borate. It is generally found in small quantities over a wide distribution.

Beryllium is generally insoluble in acids. In analytical procedures it usually accompanies aluminum, and if

undetected, will be reported as aluminum. Beryllium in solution can be determined easily by atomic absorption. High levels of aluminum and silica will interfere even in the nitrous oxide-acetylene flame, and for accurate work, aluminum and silica levels in the sample should be matched in the standards (4). The aluminum interference can also

be eliminated by addition of 2.5% (w/v) aqueous 8-hydroxy-quinoline (5).

#### Reagents

*Beryllium standard solution*, 1,000 ppm: Dissolve 2.776 g beryllium oxide (BeO) in a minimum of 50% hydrochloric acid (v/v) and dilute to one liter with distilled water.

*25% Sodium chloride solution* (w/v): Dissolve 250 g of sodium chloride (NaCl) in 750 ml of distilled water.

*CAUTION: Beryllium is potentially toxic and should be handled with care.*

#### Procedure

1. Use a 500-mg sample if beryllium content is expected to be 1% or greater. If beryllium content is expected to be less than 1%, use a 1.000-g sample.
2. Mix the sample with about 5 to 7 g of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in a platinum crucible. (See Preliminary Considerations, paragraph 5.)
3. Cover the crucible with a platinum lid. Fuse mixture over an open flame until the molten mass is clear and quiet.
4. Pour the melt onto the platinum lid for cooling. Use platinum tipped tongs to handle red hot platinum crucible.
5. Place crucible and lid in a 600-ml beaker, partially cover with a watchglass; add about 60 ml of distilled water and 20 ml of hydrochloric acid.
6. After violent action is over and fusion cake is dissolved, remove and polish crucible and lid.
7. Filter through Whatman #5 filter paper and dilute to 100 ml in a volumetric flask.
8. Determine beryllium by atomic absorption at 2349 Å using a reducing nitrous oxide-acetylene flame. Add 2 ml of NaCl solution per 100 ml to the standards and blank, and any samples which need to be diluted. Add silica and aluminum to the standards and blank, if needed. Standards should range from 1 to 5 ppm, and can be made from 0.1 to 1 ppm for use with an expanded scale.

#### Fuel Conditions

(same as for barium)

#### Remarks

*Application*—This method should be applicable to all beryllium analyses on rocks. However, we have not attempted to determine beryllium in samples which contain more

than 15% beryllium. The solution resulting from the dissolution of the fusion mass can be used for the atomic absorption analyses of other elements, providing that large amounts of sodium will not interfere. Fusion might have to be repeated for very refractory minerals. This is usually determined by visual examination of the residue following original fusion.

**Detection Limits**—With careful work, detection limits of 0.0001% beryllium can be obtained for a 1-g sample using a 10X expanded scale.

**Precision**—A relative deviation of  $\pm 3$  to 5% may be expected; however, a relative deviation of  $\pm 5$  to 10% may be expected for trace analysis.

#### References

4. Thomas, P. E., and Chummong, H., 1969, The atomic absorption determination of beryllium in beryl, *in* Resonance Lines: Monrovia, Calif., Cary Instruments Inc., v. 1, no. 2, p. 5-6.
5. Fleet, B., Liberty, K. V., and West, T. S., 1969, A study of some matrix effects in the determination of beryllium by atomic-absorption spectroscopy in the nitrous oxide-acetylene flame: *Talanta*, v. 17, p. 203-210.

### COBALT

In nature, cobalt occurs in sulfides, arsenides, arsenates, oxides, carbonates, and silicates. This element is also found in metallic form in meteoric iron. Rocks containing cobalt vary, so that no single method for solution of cobalt is universally applicable; however, as cobalt is found principally as a sulfide or arsenide, the same general method may be used in most cases. For a cobalt analysis on a silicate, an alkali fusion or the acid pressure technique (see p. 14) might be necessary.

Fleming (6) has reported interferences from high levels of iron and nickel in the determination of cobalt that can be eliminated by use of the nitrous oxide-acetylene flame. Because the cobalt determination is more sensitive in the air-acetylene flame, this flame is preferred in the absence of large relative amounts of iron and/or nickel.

#### Reagents

**Cobalt standard solution**, 1,000 ppm: Dissolve 1.000 g of cobalt metal in a minimum of 50% hydrochloric acid (v/v), Dilute to one liter with 1% hydrochloric acid (v/v).

#### Procedure

1. Use a 500-mg sample if the cobalt content is expected to be greater than 0.5%. For samples expected to be less than 0.5%, use a 1.000-g—or larger—sample size.
2. Follow steps 1 through 6 of the General Procedure for Acid Decomposition ending in a hydrochloric acid system.
3. Determine cobalt at 2407 Å using a strongly oxidizing air-acetylene flame. Prepare standards of 5, 10, 15,

and 20 ppm cobalt in 10% hydrochloric acid (v/v). Fuel Conditions

Air: 30 psi; flowmeter, 8.5, 21.5 liters/minute.

Acetylene: 10 psi; flowmeter, 8.5; 4.2 liters/minute.

#### Remarks

**Application**—Using this method, we have determined cobalt in the range of 0.05 to 5.00%. The range could be extended downward by using the expanded scales and by preparing standards in the range of 0.5 to 5.0 ppm.

**Detection Limits**—The detection limit is about 0.0005% cobalt when using a 10X expanded scale and a 2-g sample.

**Precision**—A relative deviation of  $\pm 3$  to 5% may be expected.

#### Reference

6. Fleming, H. D., 1972, Chemical and spectral interferences in the determination of cobalt in iron and steel by atomic absorption spectroscopy: *Anal. Chim. Acta*, v. 59, p. 197-208.

### COPPER

Copper generally occurs in nature as sulfide, oxide, sulfate, silicate, carbonate, and native metal. An acid dissolution of copper is applicable in most cases; if necessary, any insoluble residue may be fused with sodium carbonate. Copper is one of the elements most easily and accurately determined by atomic absorption. No interferences have been reported in the air-acetylene flame, (7) and none have been found in our laboratory. The most sensitive line for copper is 3247 Å, but other lines can be used, which although less sensitive, are occasionally convenient for copper solutions that require multiple dilutions.

#### Reagents

**Copper standard solution**, 1,000 ppm: Dissolve 1.000 g of pure copper wire in a minimum of 50% nitric acid (v/v) and dilute to one liter with distilled water.

#### Procedure

1. Use 100- to 500-mg sample if the copper content is expected to be greater than 1%. Use a 1.000- or 2.000-g sample if copper content is expected to be less than 1%.
2. Follow steps 1 through 6 of the General Procedure for Acid Decomposition ending in a nitric acid system.
3. Prepare standards of 5-, 10-, 15-, and 20-ppm copper in 10% nitric acid (v/v). Be sure all dilutions are 10% in nitric acid.
4. Determine copper at 3247Å using a strongly oxidizing air-acetylene flame.

Fuel Conditions  
(same as for cobalt)

## Remarks

*Application*—Atomic absorption is most useful for copper determinations in the range of trace to 10%.

*Detection Limit*—The detection limit is about 0.0001% copper when using a 10X expanded scale and a 2-g sample.

*Precision*—We have obtained a relative precision of  $\pm 1\%$  or better when copper is in the range of 0.10 to 10.00%. When the amount of copper rises above 10%, the relative precision is  $\pm 2$  to 3%.

## Reference

7. Walter Slavin, 1968, Atomic absorption spectroscopy: Interscience Publishers, New York, p. 103.

## IRON

Iron generally occurs in nature as oxides, sulfides, silicates, and sometimes as metal. The metal and the oxides are usually soluble in hydrochloric acid. Magnetite ( $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ ) and the iron sulfides generally require several treatments with oxidizing acid before they become solubilized. The procedure outlined below should be applicable to all iron minerals with the exception of silicates. Iron silicates are easily determined using acid pressure decomposition. (See Special Methods, Acid Pressure Decomposition Technique.)

Atomic absorption determination of iron shows good agreement ( $\pm 2\%$ ) with titration values in samples containing from 1 to 20% iron. We have found no interferences using a strongly oxidizing air-acetylene flame and a hydrochloric acid medium. However, there are some reported interferences in the literature. Large excesses of calcium, sodium,

and potassium ions have been shown by Billings (8) to produce light-scattering interferences, later termed molecular absorption interferences. Curtis (9) has demonstrated that these interferences can be kept at a minimum and may usually be considered negligible by using a strongly oxidizing air-acetylene flame, and by placing the burner 7 cm below the light path. Large relative amounts of cobalt, nickel, and copper have been shown by Ottaway, Coker, Rowston, and Bhattarai (10) to interfere with the iron determination. The authors have suggested the use of a 5% aqueous solution of 8-hydroxyquinoline as a releasing agent in cases where extreme accuracy is desired. For routine assays, the interferences are slight in hydrochloric acid media.

## Reagents

*Iron standard solution*, 1,000 ppm: Dissolve 1.000 g of pure iron wire in a minimum of 50% hydrochloric acid (v/v), and dilute with distilled water to one liter.

*Hydrogen peroxide*, commercial reagent, 30%.

## Procedure

1. Weigh out 250-mg to 1.000-g sample into a 400-ml beaker.
2. Add 10 ml of hydrochloric acid and 2 ml of 30% hydrogen peroxide. Cover with a watchglass and digest for 30 minutes.
3. Inspect the residue carefully. If sample appears dissolved (white particles of silicate maybe present), reduce the volume of hydrochloric acid to 10 ml by heating, cool, and add 20 ml of distilled water. Transfer to a 100-ml volumetric flask, bring to volume with distilled water, and allow the solids to settle. If any black particles remain in the residue, follow steps 1-5 of the General Procedure for Acid Decomposition ending in a hydrochloric acid system.
4. Prepare standards of 5-, 10-, 15-, and 20-ppm iron in 10% hydrochloric acid (v/v). Any dilutions should be 10% in hydrochloric acid also.
5. Determine iron at 2483 Å using a strongly oxidizing air-acetylene flame. Position burner 7 cm below the light path.

## Fuel Conditions

(same as for cobalt)

## Remarks

*Application*—Iron can be determined with good precision from trace amounts to 50%. The precision decreases with decreasing amounts of iron.

*Detection Limits*—The detection limit is about 0.0005% when using a 1-g sample and the 10X expanded scale.

*Precision*—A relative deviation of  $\pm 1$  to 4% may be expected.

## References

8. Billings, G. K., 1965, Light scattering in trace element analysis by atomic absorption: Atomic Absorption Newsletter, v. 4, no. 10, p. 357-361.
9. Curtis, K. E., 1969, Interferences in the determination of iron by atomic absorption spectrophotometry in an air-acetylene flame: Analyst, v. 94, p. 1068-1071.
10. Ottaway, J. M., Coker, D. T., Rowston, W. B., and Bhattarai, D. R., 1970, The interference of cobalt, nickel, and copper in the determination of iron by atomic absorption spectrophotometry in an air-acetylene flame: Analyst, v. 95, p. 567-573.

## LEAD

Lead most commonly occurs in nature as the sulfide, sulfate, and carbonate. Lead sulfide is not easily decomposed and may require several treatments with acid. The presence of dark particles in the residue usually indicates the need for further acid treatment. Lead sulfide ores

containing more than 3% lead, and samples containing lead sulfate, should be analyzed by the method listed in Special Methods section for high grade lead and zinc ores. Lead sulfate is only slightly soluble in perchloric or nitric acids, and in the case of lead sulfide, some sulfate will form by the oxidizing action of acids, and can cause some precipitation of lead sulfate.

Atomic absorption probably provides the most satisfactory method for lead determinations. In general, there are no chemical interferences in the air-acetylene flame (11). Anions that form insoluble lead precipitates are an exception.

#### Reagents

*Lead standard solution*, 1,000 ppm: Dissolve 1.598 g of lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ ) in a minimum amount of 50% nitric acid (v/v) and dilute to one liter with distilled water.

#### Procedure

1. Use a 250- to 500-mg sample if lead content is expected to be 1% or greater. For samples expected to run less than 1% lead, use a 1.000- or 2.000-g sample size.
2. Weigh sample into a 400-ml beaker.
3. Add 15 ml of nitric acid and 10 ml of perchloric acid. Cover and reflux for about an hour on a hotplate.
4. Remove cover and take to dryness. If any dark particles remain, repeat the digestion with nitric and perchloric acids and evaporate to dryness.
5. Cool, add 10 ml of nitric acid and boil to break up the salt cake. Dilute to volume in a 100-ml volumetric flask with distilled water. Allow solids to settle.
6. Determine lead by atomic absorption at 2833 Å with a strongly oxidizing air-acetylene flame. Be sure that the blank, standards (5-, 10-, 15-, and 20-ppm), and any dilutions contain 10 ml of nitric acid per 100 ml volume.

#### Fuel Conditions

(same as for cobalt)

#### Remarks

*Application—Lead* carbonates, oxides, and sulfides containing less than 3% lead can easily be determined by this procedure. Silicates should be decomposed by carbonate fusion. Use an acid leach on the sample before fusion, then add the acid leach liquid to the fusion melt. The acid bomb decomposition technique is not recommended, since lead fluoride is only slightly soluble. Lead sulfates and lead sulfide ores should be analyzed by the method listed in the Special Methods section for high grade lead and zinc ores.

*Detection Limits—Detection* limit is about 0.001% using the 10X scale and a 2-g sample.

*Precision—A* relative deviation of  $\pm 2$  to 5% may be expected.

#### Reference

11. Slavin, W., 1968, Atomic absorption spectroscopy: Interscience Publishers, New York, p. 119.

#### NICKEL

In nature, nickel is found in arsenates, antimonates, silicates, sulfides, phosphates, oxides, and also as  $\text{FeNi}_2$  and  $\text{FeNi}_3$ . Most nickel compounds are brought into

solution by treatment with acids, but some refractory rocks (silicates, for example) require fusion or acid pressure decomposition.

Atomic absorption provides a fast, accurate method for the determination of nickel. The air-acetylene flame must be strongly oxidizing to avoid interference from iron and chromium.

#### Reagents

*Nickel standard solution*, 1,000 ppm: Dissolve 1.000 g of pure nickel wire in a minimum of 50% nitric acid (v/v) and dilute to one liter with distilled water.

#### Procedure

1. Use a 0.500-g sample or less if nickel content is expected to be a greater than 1% and a 1.000- or 2.000-g sample if nickel content is expected to be less than 1%.
  2. Follow steps 1 through 5 of the General Procedure for Acid Decomposition
  3. Determine nickel by atomic absorption at 2320 Å using a strongly oxidizing air-acetylene flame. Standards should be in the range of 5 to 20 ppm.
- Fuel Conditions  
(same as for cobalt)

#### Remarks

*Application—This* procedure applies to nearly all nickel-containing compounds, except for refractory oxides and silicates.

*Detection Limits—The* detection limit is about 0.0025% when using a 2-g sample and the 10X expanded scale.

*Precision—A* relative deviation of  $\pm 2$  to 5% may be expected.

#### TELLURIUM

Tellurium occurs, in nature as the native element, and in the tellurides of gold, silver, lead, bismuth, copper, mercury, and nickel, and as tellurites and tellurates. The native element is soluble in hot sulfuric acid, and most tellurides, tellurites, and tellurates are soluble in nitric acid. Special care should be taken in the determination of

tellurium since losses can occur with hot, concentrated, hydrochloric acid due to volatilization.

This procedure was written for determining trace (ppm) amounts of tellurium in rock samples. The separation of tellurium is necessary because the large sample size (10 g) causes problems with the atomic absorption determination (clogged aspirator, unstable readings, etc.). This separation step is unnecessary if the tellurium is in the percent range. The silver is added to act as a collector for the small amounts of tellurium.

#### Reagents

*Tellurium standard solution*, 1,000 ppm: Dissolve 1.000 g of tellurium metal by slowly adding a minimum volume of concentrated nitric acid. Dilute to about 50 ml with distilled water. Redissolve the precipitate with a minimum of hydrochloric acid. Heat to expel the oxides of nitrogen, cool, and dilute to one liter with 1% hydrochloric acid (v/v).

*Silver sulfate solution*, 1 mg Ag/ml; dissolve 1.44 g of silver sulfate ( $\text{Ag}_2\text{SO}_4$ ) in one liter of distilled water.

20% *Stannous chloride solution* (w/v): Dissolve 20 g of stannous chloride ( $\text{SnCl}_2$ ) in 80 ml of concentrated hydrochloric acid.

#### Procedure

1. Weigh a 10-g sample into a 400-ml beaker.
2. Wet the sample with distilled water and add 5 ml of nitric acid, 3 ml of hydrofluoric acid, and 15 ml of sulfuric acid. Swirl to mix.
3. Evaporate the solution to dryness and bake to remove the sulfuric acid.
4. Cool. Add 5 ml of hydrochloric acid, about 10 ml of distilled water, and warm to effect the solution of soluble salts.
5. Add 1 ml of the silver sulfate solution and swirl to mix.
6. Filter the solution through Whatman #5 filter paper into a 400-ml beaker. Wash the residue with distilled water. Volume at this point should be about 100 ml.
7. Add 10 ml of the stannous chloride solution and swirl the beaker. The silver and tellurium will be reduced to metal and be precipitated.
8. Digest the solution for a half hour on the hotplate.
9. Filter through glass filter paper using suction.
10. Wash the beaker and filter apparatus 5 times with 1:4 hydrochloric acid.
11. Add 1 ml of hot nitric acid to dissolve the tellurium, and wash with several ml of distilled water. Repeat.
12. Rinse the solution carefully back into the original beaker and take to dryness.
13. Add several drops of hydrochloric acid and 5 ml of water; warm to dissolve the soluble salts.
14. Transfer to a 10-ml volumetric flask and bring to volume with distilled water.

15. Determine tellurium by atomic absorption at 2143 Å using an oxidizing air-acetylene flame and the 10X expanded scale. Standards should range from 1 to 5 ppm.

#### Fuel Conditions

(same as for cobalt)

#### Remarks

*Application*—This procedure is applicable for determination of trace amounts of tellurium in rock samples.

*Detection Limit*—The detection limit is about 0.0001% tellurium.

*Precision*—A relative deviation of  $\pm 10\%$  may be expected.

### ZINC

Zinc is found in nature only in the combined form, commonly as sulfide, carbonate, oxide, and silicate. Treatment of the sulfide, oxide, and carbonate minerals with an oxidizing acid will readily extract the zinc. If a zinc determination is required on a silicate, the acid pressure decomposition method is recommended.

Atomic absorption is extremely sensitive for zinc, and is rapidly replacing traditional assay methods. There are conflicting reports of interferences in the determination of zinc in the literature. Billings (8) reports interference from as low as 500-ppm calcium, and also from sodium, potassium, magnesium, and iron in an air-propane flame. David (12) reports no interference on 1 ppm-zinc by 7,800-ppm sodium, 10,000-ppm potassium, 8,000-ppm calcium, and 4,000-ppm magnesium in an air-acetylene flame. Platte and Marcy (13) found no interference on

1 ppm zinc from 1,000 ppm of iron, calcium or sodium in the air-acetylene flame. In this laboratory we find sodium interference on zinc only if the sodium/zinc ratio is 10,000 to 1 or greater. The same is true for calcium. The conflicting reports in the literature are probably due to flame and fuel differences.

#### Reagents

*Zinc standard solution*, 1,000 ppm: Dissolve 1.000 g of pure zinc metal in a minimum volume of 50% hydrochloric acid (v/v) and dilute to one liter with distilled water.

#### Procedure

1. Weigh out 250- to 500-mg sample for concentrates and 1.000- or 2.000-g sample for materials expected to be low in zinc.
2. Follow steps 1 through 5 of the General Procedure for Acid Decomposition.
3. Determine the zinc by atomic absorption at 2139 Å using a strongly oxidizing air-acetylene flame.

- 4 Match the amount and type of acid in the blank and standards (1 to 3 ppm) with that in the sample. If sodium calcium is high in the sample relative to zinc (10,000 to 1), the sodium or calcium value should be matched in the blank and standards.

#### Fuel Conditions

(same as for cobalt)

#### Remarks

*Application*—This method applies to the determination of sulfides, carbonates, and oxides.

*Detection Limits*—The detection limit is about 0.0025% zinc when using a 2-g sample and the 10X expanded scale.

*Precision*—A relative deviation of  $\pm 3$  to 5% may be expected.

#### References

8. Billings, G. K., 1965, Light scattering in trace element analysis by atomic absorption: Atomic Absorption Newsletter, v. 4, no. 10, p. 357-361.
12. David, D. J., 1958, Determination of zinc and other elements in plants by atomic absorption spectroscopy: Analyst, v. 83, p. 655-661.
13. Platte, J. A., and Marcy, V. M., 1965, Atomic absorption spectrophotometry as a tool for the water chemist: Atomic Absorption Newsletter, v. 4, p. 289-292.

or

zinc in

## SPECIAL METHODS

### ACID PRESSURE DECOMPOSITION TECHNIQUE FOR SILICATE ANALYSIS

Silicates are well known for their extreme insolubility. Most decomposition methods use an alkali fusion or hydrofluoric acid treatment, and in many cases, a complete analysis requires both methods. These methods also present problems when using the resulting solutions for atomic absorption analysis (see Preliminary Considerations). The following decomposition method of Bernas (1) is simple, rapid, and accurate. It makes use of a sealed Teflon-lined steel bomb and a fluoboric-boric acid system, which results in a salt-free single matrix system. This matrix system eliminates the need for different reagents to overcome the various types of interferences or having to match sample and standards with respect to the other matrix constituents. This matrix system also contributes to the signal stability.

Atomic absorption determinations for silicon, aluminum, titanium, vanadium, iron, calcium, magnesium, sodium, and potassium can all be performed on a single solution. In our laboratory, determinations were not done for titanium and vanadium.

#### Reagents and apparatus

*Aluminum standard solution*, 1,000 ppm: Dissolve 1.000 g of pure aluminum metal in a minimum amount of hydrochloric acid using a small drop of mercury as a catalyst. Dilute to one liter with 1% hydrochloric acid (v/v).

*Calcium standard solution*, 1,000 ppm: Add 50 ml of distilled water to 2.497 g of primary standard calcium carbonate ( $\text{CaCO}_3$ ). Then add dropwise a minimum amount of hydrochloric acid to completely dissolve the  $\text{CaCO}_3$ . Dilute to one liter with distilled water.

*Iron standard solution*, 1,000 ppm: Dissolve 1.000 g of pure iron wire in 50 ml of 50% nitric acid (v/v). Dilute to one liter with distilled water.

*Magnesium standard solution*, 1,000 ppm: Dissolve 1.000 g of pure magnesium ribbon in a minimum of 50% hydrochloric acid (v/v). Dilute to one liter with distilled water.

*Potassium standard solution*, 1,000 ppm: Dissolve 1.907 g of potassium chloride (KCl) in one liter of distilled water.

*Silica standard solution*, 1,000 ppm: Dissolve 0.2139 g of silicon dioxide ( $\text{SiO}_2$ ) in 6 ml of 50% hydrofluoric acid (v/v) in a polystyrene vial. Close the vial with a polystyrene cap and leave it standing at room temperature until dissolution is complete and the solution is at room temperature. Add 2.8 g of boric acid, 50 ml of distilled water, and stir to dissolve. Dilute to 100 ml with distilled water.

*Sodium standard solution*, 1,000 ppm: dissolve 2.542 g of sodium chloride (NaCl) in one liter of distilled water.

*Fluoboric-boric acid solution*: Dissolve 28 g of boric acid ( $\text{H}_3\text{BO}_3$ ) in distilled water, add 30 ml of hydrofluoric acid and dilute to one liter with distilled water.

*Decomposition vessel*: The decomposition vessel has a volume of about 30 ml, it is made of stainless steel with a Teflon liner, and has a screw cap which has a Teflon sealing disc. The contact area between the acids and the vessel is all Teflon. This vessel is pictured in the referenced article (1).

*Polystyrene beakers*, 250- or 500-ml size.

Each of the standard solutions used for calibration graphs should contain 3.0 ml of hydrofluoric and 2.8 g of boric acid per 100 ml of solution. Any dilution of the samples should be done with the fluoboric-boric acid solution.

#### Procedure

1. Transfer 100 to 500 mg of sample into the decomposition vessel.
2. Add 0.5 to 1.0 ml of aqua regia as a wetting agent, making certain that the sample has become thoroughly wetted.
3. Then add 3.0 ml of hydrofluoric acid and close the vessel by hand-tightening the screw cap. Be careful not to seal it too tightly or it will be extremely difficult to remove.
4. Place the vessel into a drying oven at 120°C. for 30 to 40 minutes. Let it cool to room temperature.
5. Unscrew the lid and examine the solution. The sample should be completely decomposed, although there might be some precipitated metal fluorides.
6. Transfer the decomposed sample solution and any precipitate to a 250-ml polystyrene beaker, with the aid of about 5 ml of distilled water.
7. Add 2.8 g of boric acid and stir with a Teflon stir-bar to dissolve the boric acid and any precipitated metal fluorides, warming slightly if necessary.
8. Dilute the sample solution to about 50 ml with distilled water. Transfer to a 100-ml volumetric flask, bring to volume with distilled water, and store in a polyethylene container.
9. Determine all the constituents by atomic absorption using this solution.

#### Remarks

*Application*—This method should be applicable to the decomposition and atomic absorption determination of most of the refractory minerals associated with silicate rocks. In a more recent publication, the author (14) reports successfully determining in silicate rocks the above mentioned elements and also antimony, barium, cobalt, copper, lead, manganese, molybdenum, nickel, and zinc.

Fuel and analytical conditions

Element→	Al	Si	Ca	Mg	Fe	K	Na
Wavelength Å	3093	2516	4227	2852	2483	7665	5890
Standards, ppm	20-200	50-200	1-8	0.5-2.0	1-10	1-10	0.5-3.0
Acetylene, 10 psi flowmeter liters/min.	13.0 7.0	13.0 7.0	10.5 5.4	10.0 5.0	8.5 4.2	8.5 4.2	8.5 4.2
Air, 30 psi flowmeter liters/min.					8.5 21.5	8.5 21.5	8.5 21.5
Nitrous oxide, 30 psi flowmeter liters/min.	5.5 11.7	5.5 11.7	5.0 10.7	5.5 11.7			

We have successfully determined calcium in samples containing up to 20% calcium. In other words, calcium fluoride is soluble in the fluoboric-boric acid medium.

**Detection limits**—Detection limits have not been established, but they should be similar to detection limits for these elements in other matrices.

**Precision**—For silica and alumina we have obtained a relative deviation of  $\pm 0.5\%$ , for calcium, magnesium and iron a relative deviation of  $\pm 1$  to 2%, and for potassium and sodium a relative deviation of  $\pm 3$  to 4%.

#### References

1. Bernas, Bedrich, 1968, A new method for decomposition and comprehensive analysis of silicates by atomic absorption spectrometry; *Anal. Chem.* v. 40, no. 11, p. 1682-1686.
14. Bernas, Bedrich, 1973, Acid pressure decomposition device for interference-free A A analysis; American Laboratory, International Scientific Communications, Inc., v. 5, no. 8, p. 41-43.

#### ANALYSIS OF FLUORITE FOR CALCIUM CARBONATE AND CALCIUM FLUORITE

Calcium fluoride is usually determined by fluorine analysis. No matter which method of fluorine analysis is used—distillation and titration, alkali fusion and specific ion electrode, or gravimetric—the process is lengthy, and requires familiarity and experience on the part of the analyst. The following method is based on the separate determinations of calcium as the carbonate and as the fluoride. The assay is *not valid* when calcium is present in the ore in any other form, but gives excellent results when applicable. It was developed to answer the need for a fast analysis of flotation tests. With this method, a dozen samples can be assayed in duplicate in less than 3 hours by a single analyst.

There are reported interferences in the calcium determination in the air-acetylene flame from sulfate, phosphate, silicate, and aluminum. These interferences can be made negligible by using a slightly reducing flame and lowering the burner head 2 cm lower than its usual position immediately under the light beam (15).

#### Reagents

**Calcium standard solution**, 1,000 ppm: Wet 2,497 g of primary standard calcium carbonate ( $\text{CaCO}_3$ ) with distilled water and add dropwise a minimum of hydrochloric acid (approximately 10 ml) to dissolve the  $\text{CaCO}_3$ . Dilute to one liter with distilled water.

**5% Acetic acid solution**, (v/v): Dilute 50 ml of concentrated acetic acid to 1,000 ml with distilled water.

#### Procedure

1. Weigh the sample (100-mg sample for concentrates, 250- to 1,000-mg sample for ores and tails) into a 400-ml beaker.
2. Add 15 ml of the acetic acid solution, place the beaker on the hotplate and bring just to the first boil.
3. Filter immediately through Whatman #5 filter paper into a 100-ml volumetric flask. Rinse the residue carefully with distilled water.
4. Bring the solution to volume and determine calcium by atomic absorption at 4227 Å in a slightly reducing air-acetylene flame, using the three-slot burner. Lower the burner head 2 cm lower than its usual position. Match the acetic acid in the blank and standards (2 to 10 ppm) with that of the sample. Report the calcium as the carbonate.
5. Return the precipitate and the filter paper to the original beaker. Add 15 ml of nitric acid and 10 ml of perchloric acid. *Use caution with perchloric acid and organic matter!*
6. Cover the beaker and heat until the solution is clear and colorless.
7. Remove the cover and evaporate almost to dryness. Cool.
8. Bring to volume in a 100-ml volumetric flask with distilled water. Allow any solids to settle.
9. Determine calcium by atomic absorption at 4227 Å in a slightly reducing air-acetylene flame, using a three-slot burner. Lower the burner head 2 cm lower than its usual position. It is not necessary to add perchloric acid to the standards (2 to 10 ppm) and blank because the sample will have to be diluted enough to make the amount of acid negligible.



**Fuel Conditions**

Air: 30 psi; flowmeter, 7.0; 17.5 liters/minute.  
 Acetylene: 10 psi; flowmeter, 8.5; 4.2  
 liters/minute.

**Remarks**

*Application*—This method applies to those fluorite ores which contain calcium only as the carbonate and the fluoride.

*Detection limits*—The detection limit is easily 0.1% calcium and lower limits are not needed.

*Precision*—A relative deviation of  $\pm 2\%$  or better may be expected.

**Reference**

15. Popham, R. E., and Schrenk, W. G., 1968, A new look at calcium flame interferences: Develop. Appl. Spectrosc. 7 A, p. 189-200.

### COPPER OXIDE IN ORES AND CONCENTRATES

The term copper oxide usually refers to the acid-leachable copper in an ore. The leach conditions then determine the amount of copper oxide reported, which

will vary with the conditions. In this method, copper oxide is defined as that copper which will dissolve in 50 ml of 10% sulfuric acid in a half hour at room temperature (16).

**Reagents**

10% *Sulfuric acid* (v/v): Add 100 ml of concentrated sulfuric acid *slowly*, with stirring, to 900 ml of distilled water.

**Procedure**

1. Weigh a 1.000-g sample into a 250-ml beaker.
2. Add 50 ml of the sulfuric acid solution.
3. Swirl gently and allow the solution to stand at room temperature for a half hour, with occasional swirling.
4. Filter the solution into a 100-ml volumetric flask. Dilute to volume with distilled water.
5. Determine copper by atomic absorption at 3247 Å, using an oxidizing air-acetylene flame. Prepare standards of 5-, 10-, 15-, and 20-ppm copper in 5% sulfuric acid (v/v).

Fuel Conditions  
 (same as for cobalt)

**Remarks**

*Application*—This method differentiates between acid-leachable and nonleachable copper in ores and concentrates. This assay is frequently required in mining and metallurgical analysis.

*Detection Limits*—Values of 0.01% copper are easily reached without using the expanded scales. Lower limits can be reached but are not usually necessary.

*Precision*—A relative deviation of  $\pm 1$  to 3% may be expected.

**Reference**

16. Keffer, Robert, 1928, Methods in non-ferrous metallurgical analysis: New York, McGraw-Hill Book Co., p. 103.

### LEAD AND ZINC IN HIGH GRADE ORES

Acid treatment of an ore is sufficient for lead oxides, carbonates, and low grade sulfide ores. However, if lead is present as the sulfate or present in large amounts as the sulfide, the following method of solution is recommended: This method utilizes the fact that lead acetate is a very soluble lead salt, i. e., lead sulfate is highly soluble in ammonium acetate.

The concentration of ammonium acetate in the samples and standards should be closely matched. If not enough ammonium acetate is present in the dilutions, low values for lead may result.

**Reagents**

*Lead standard solution*, 1,000 ppm: See lead standard under Lead in General Methods section.

50% *Hydrochloric acid* (v/v): Dilute concentrated hydrochloric acid 1:1 with distilled water.

*Ammonium acetate solution*: Mix ammonium hydroxide (NH<sub>4</sub>OH), acetic acid (CH<sub>3</sub>COOH), and distilled water 1:1:1 by volume.

**Procedure**

1. Weigh a 500-mg sample into a 250-ml Phillips flask.
2. Add 15 ml of concentrated hydrochloric acid and boil until the volume is about 10 ml.
3. Add 10 ml of concentrated nitric acid and continue boiling until most of the nitrogen dioxide has been evolved (reddish-brown gas).
4. Add about 0.2 g of potassium perchlorate and evaporate the solution to dryness. Do not bake.
5. Add 20 ml of 50% hydrochloric acid, bring to a boil, and boil until the cake is well dissociated.
6. Add 45 ml of ammonium acetate and again bring to a boil.
7. Transfer to a 100-ml volumetric flask, cool, dilute to volume with distilled water, and mix.
8. After the solids have settled, determine lead by atomic absorption at 2833 Å with an oxidizing air-acetylene flame. Be certain that the blank, standards (5-, 10-, 15-, and 20-ppm) and any dilutions are in 10% hydrochloric acid and 45% ammonium acetate solution. Use fuel conditions listed previously for lead.

acetylene flame. Again, be certain that the blank and standards (1, 2, 3, 4 ppm) are in 10% hydrochloric acid and 45% ammonium acetate solution. Use fuel conditions listed previously for zinc.

#### Remarks

*Application*—This method was written specifically for determining lead and zinc in high grade ores, although it would apply to most lead and zinc samples. However, the general acid decomposition methods for lead and zinc listed under General Methods are faster, and are preferable whenever applicable. Zinc would probably be determined by this method only when lead and zinc determinations are required on the same high grade lead ore. Lead will be in solution over a range of 0-40% using the ammonium acetate-hydrochloric acid mixture.

*Precision*—For samples containing between 10 and 30% lead, a relative deviation of  $\pm 2\%$  may be expected. For samples containing between 3 and 25% zinc, a relative deviation of  $\pm 3$  to 4% may be expected.

#### References

Thomas, Byron G., 1971, Determination of silver, lead, and zinc in high grade ores: Atomic Absorption Newsletter, v. 10, p. 73-74.

#### MANGANESE IN MANGANESE ORES

Manganese ores are generally soluble in hot hydrochloric acid-hydrogen peroxide solution. If a colored residue remains after acid-peroxide treatment, it should be fused with sodium carbonate and sodium peroxide (3:1) and the melt added to the acid solution.

Manganese in solution can be determined easily by atomic absorption spectrometry. The only reported interference is from silica (13), (17), and this can be overcome easily by the addition of 200 mg/ml of calcium (13) or by the use of a three-slot burner (17). In this procedure it is not likely that silica will interfere, since it is insoluble, unless an alkali fusion is needed.

#### Reagents

*Manganese standard solution, 1,000 ppm:* Dissolve 1.000 g of pure manganese metal in a minimum volume of 50% nitric acid (v/v). Dilute to one liter with 1% hydrochloric acid.

*Hydrogen peroxide solution, 30% (w/w).*

#### Procedure

1. Weigh a 250- to 500-mg sample into a 400-ml beaker.
2. Add 20 ml of hydrochloric acid and 5 ml of hydrogen peroxide.
3. Cover and digest for about 30 minutes.
4. Remove the cover and boil for about 5 minutes.

1. All the manganese should now be in solution.

Evaporate the solution almost to dryness. If any colored residue remains, add 10 ml of perchloric acid and heat to strong perchloric acid fumes. If any colored residue still remains, filter the solution and

fuse the residue with 3 parts of sodium carbonate and 1 part of sodium peroxide. Add the melt to the acid filtrate, adding more acid as necessary.

2. Bring the solution to 100-ml volume in a volumetric flask with distilled water.

3. Determine manganese by atomic absorption at 2795 Å using a strongly oxidizing air-acetylene flame.

Prepare standards in the range of 1 to 10 ppm. If a carbonate fusion was necessary, the blank and standards should contain a similar amount of sodium. In order to avoid silicate interference in the case of a carbonate fusion, add 200 µg/ml of calcium to the sample, blank, and standards or use the three-got burner.

Fuel Conditions  
(same as for cobalt)

#### Remarks

*Application*—The acid-peroxide dissolution procedure applies to most manganese minerals, although for some manganese silicates and certain other refractory minerals, an oxidizing alkali fusion is necessary.

*Detection Limits*—The detection limit for this method is about 0.002% with a 500-mg sample and the 10X expanded scale.

*Precision*—A relative deviation of  $\pm 3$  to 5% may be expected.

#### References

13. Platte, J. A., and Marcy, V. M., 1965, Atomic absorption spectrophotometry as a tool for the water chemist: Atomic Absorption Newsletter, v. 4, no. 6, p. 289-292.
17. Belcher, C. B., and Kinson, K., 1964, The determination of manganese in iron and steel by atomic absorption spectrophotometry: Anal. Chim. Acta, v. 30, p. 483.

#### MERCURY IN ORES AND CONCENTRATES

Mercury is found in quartz, sandstone, schists, iron pyrites, copper sulfides, and bituminous substances. The most important mineral is cinnabar (HgS); minor minerals are calomel (Hg<sub>2</sub>Cl<sub>2</sub>) and tiemannite (HgSe). It is also found in small quantities as amalgams with silver, gold, and tellurium and sometimes as native mercury.

Currently, there is considerable interest in mercury analysis of ores and concentrates, because of the possibility of releasing mercury into the environment by mining and smelting operations. This type of analysis requires the determination of mercury in the ppb range, which has recently been made possible by the development of a flame-less atomic absorption technique (18).

Mercury is easily brought into solution with oxidizing acids, but is extremely volatile, and the usual methods of acid dissolution result in loss of mercury. The method described below, based on the acid pressure decomposition technique of Bernas (1), does not result in loss of mercury.

#### Reagents

50% *Sulfuric acid* (v/v): Slowly, with stirring, add 250 ml of concentrated sulfuric acid to 250 ml of distilled water.

*Potassium permanganate*,  $\text{KMnO}_4$ .

10% *Stannous chloride* (w/v): Dissolve 20 g of stannous chloride ( $\text{SnCl}_2$ ) in 40 ml of hydrochloric acid and dilute to 180 ml.

25% *Hydroxylamine hydrochloride* (w/v): Dissolve 50 g of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) in 150 ml of distilled water.

*Mercury standard solution*, 1,000 ppm: Dissolve 1.354 g of mercuric chloride ( $\text{HgCl}_2$ ) in distilled water, add 10 ml of nitric acid and dilute to one liter with distilled water.

*Mercury working standard*, 1 ppm (1 pg/ml): Dilute 10 ml of the 1,000 ppm standard to one liter with distilled water. Dilute 10 ml of this standard (10 ppm) to 100 ml with distilled water. Prepare fresh daily. (If the working standard is allowed to stand for about 5 days in a glass container, the mercury will reach an equilibrium between the water and the glass and a new solution placed in the glass container will remain stable for months.)

#### Apparatus

*Decomposition vessel*: Volume of about 30 ml. Made of stainless steel with a Teflon liner; screw cap has Teflon sealing disk. The contact area between the acid and the vessel is all Teflon. This vessel is described more completely in the referenced article (1).

*Flameless atomic absorption apparatus*: Described and pictured in the referenced article (18).

NOTE: All glassware used in this analysis must be rinsed with nitric acid and distilled water immediately prior to use.

#### Procedure

1. Weigh out 100 to 2,000 mg of sample and place in the Teflon-lined steel bomb. (Sample should contain about 1 pg of mercury.)
2. Add 10 ml of 50% sulfuric acid (v/v), 0.5 ml hydrofluoric acid, and 0.5 g of  $\text{KMnO}_4$ . (For sulfide ores and concentrates increase this to 1 g of  $\text{KMnO}_4$  and take as small a sample size as possible bearing in mind the sample should contain at least 0.1  $\mu\text{g}$  mercury.)
3. Seal immediately.
4. Place the bomb in an oven at  $150^\circ\text{C}$  for one hour.
5. While the sample is heating, set up the apparatus for

flameless atomic absorption.

6. Prepare 3 blanks and 5 standards (.05, 0.1, 0.3, 0.5, and 1.0  $\mu\text{g}$ ) containing 10 ml of 50% sulfuric acid and 0.5 g of  $\text{KMnO}_4$  in 250-ml round-bottom flasks with ground glass joints to fit flameless atomic absorption apparatus. Add 2 ml of 25% hydroxylamine hydrochloride to each flask and dilute to 100 ml.
7. Remove the bomb from the oven and let it cool to room temperature.
8. While the bomb is cooling, attach a round-bottom flask containing one of the blanks to the flameless atomic absorption apparatus, add 10 ml of 10% stannous chloride solution, close the system and measure the absorption at 2537 Å. If the apparatus has not been used for several days, run several blanks to make sure there is no residual mercury.
9. Reduce the standards and obtain a standard curve.
10. Add 2 ml of 25% hydroxylamine hydrochloride to the solution in the bomb and mix. Transfer the solution to a round-bottom flask.
11. Add 10 ml of 10% stannous chloride, close the system and measure the absorption at 2537 Å.

#### Remarks

*Application*—This method is applicable to ores and concentrates. It should be applicable to all solid samples, but coal is an exception.

*Detection limit*—The detection limit is about 5 ppb using a 2-g sample and the 10X expanded scale.

*Precision*—A relative deviation of  $\pm 5\%$  may be attained.

#### References

18. Hatch, W. R., and Ott, W. L., 1968, Determination of sub-microgram quantities of mercury by atomic absorption spectrometry: *Anal. Chemistry*, v. 40 no. 14, p. 2085-2089.
1. Bernas, Bedrich. 1968, A new method for decomposition and comprehensive analysis of silicate by atomic absorption spectrometry: *Anal. Chemistry*, v.40, no. 11, p. 1682-1686.

#### MOLYBDENUM IN MOLYBDENITE

Molybdenite ( $\text{MoS}_2$ ), is relatively insoluble mineral. Other molybdenum-containing minerals dissolve readily in aqua regia, so although this procedure is written specifically for  $\text{MoS}_2$ , it should be applicable to most rocks containing molybdenum.

Molybdenum requires a fuel-rich nitrous oxide-acetylene flame to achieve maximum sensitivity, Aluminum ions must be present in the solution to prevent molybdenum from forming a refractory oxide in the flame (19). The amount of aluminum ions needed varies in direct proportion to other refractory elements present, such as calcium, and a trial-and-error method is needed for each ore to determine the minimum amount of aluminum needed.

For the determination of molybdenum in the presence of extremely large amounts of other ions (for example, the determination of molybdenum in copper or iron concen-

trates), Mostyn and Cunningham (20) recommend the use of 2% ammonium chloride instead of aluminum as an interference suppressing agent. However, this was determined with an air-acetylene flame and a wavelength of 3798 Å.

#### Reagents

*Molybdenum standard solution*, 1,000 ppm: Dissolve 1.500 g of pure molybdenum oxide ( $\text{MoO}_3$ ) in a minimum amount of 50% ammonium hydroxide (v/v), and dilute to one liter with distilled water.

*2.5% Aluminum solution* (w/v): Dissolve 123.6 g of aluminum chloride ( $\text{AlCl}_3$ ) in 875 ml of distilled water.

#### Procedure

1. Weigh out 0.500 to 1.000 g of sample (depending on the amount of molybdenum expected) into a 400-ml beaker.
2. Add 5 ml of nitric acid, 15 ml of hydrochloric acid, and 10 ml of perchloric acid. Cover and digest on a hotplate for 40 minutes.
3. Remove the cover and evaporate to dryness. If any black particles remain, add 10 ml of perchloric acid and again evaporate to dryness.
4. Add 20 ml of hydrochloric acid and 20 ml of distilled water and boil for 10 minutes.
5. Filter the solution into a 100-ml volumetric flask, add 2.5 ml of the aluminum solution (more may be needed, see General Discussion), and dilute to volume with distilled water.
6. Determine the molybdenum by atomic absorption at 3133 Å using a fuel-rich nitrous oxide-acetylene flame (adjust the fuel so that a half-inch "red feather" is present). Blank, standards (10 to 100 ppm), and sample must contain the same amount of the aluminum solution per 100 ml volume.

#### Fuel Conditions

Nitrous oxide: 30 psi; flowmeter, 5.0; 10.8 liters/minute.

Acetylene: 10 psi; flowmeter, 13.0; 7.0 liters/minute.

#### Remarks

*Application*-This procedure is applicable to almost all rocks, providing they contain at least 0.005% molybdenum.

*Detection Limit*-The detection limit is about 0.005% using a 2 g sample and the 10X scale.

*Precision*-A relative deviation of  $\pm 5$  to 10% may be expected.

#### References

19. McIsaac, C. L., 1969, Determining  $\text{MoS}_2$  in siliceous ores with atomic absorption: Eng. and Mining Jour., no. 1, p. 55-56.
20. Mostyn, R. A., and Cunningham, A. F., 1966, Determination of molybdenum in ferrous alloys by atomic absorption spectrometry: Anal. Chemistry, v. 38, no. 1, p. 121-123.

## MOLYBDENUM OXIDE IN ORES AND CONCENTRATES

Because molybdenum sulfides and oxides, with the exception of  $\text{MoO}_3$ , are not soluble in cold dilute acids, a separation of  $\text{MoO}_3$  from an ore is possible by leaching with a cold dilute acid.

The determination of molybdenum by atomic absorption requires a fuel-rich nitrous oxide-acetylene flame to achieve maximum sensitivity. Aluminum ions must be present in the solution to prevent molybdenum from forming a refractory oxide in the flame.

#### Reagents

*10% Sulfuric acid* (v/v): Slowly, with stirring, add 100 ml of sulfuric acid to 900 ml of distilled water.

*Molybdenum standard solution*, 1,000 ppm: See Molybdenum in Molybdenite.

*2.5% Aluminum solution* (w/v): See Molybdenum in Molybdenite.

#### Procedure

1. Weigh a 1.000- or 2.000-g sample into a 250-ml beaker.
2. Add 50 ml of 10% sulfuric acid and swirl to mix.
3. Let the mixture stand for 30 minutes, swirling occasionally.
4. Filter the solution through Whatman #5 filter paper and discard the precipitate.
5. Add 2.5 ml of the aluminum solution and dilute to 100 ml volume.
6. Determine molybdenum by atomic absorption at 3133 Å using a fuel-rich nitrous oxide-acetylene flame. Prepare standards in the range of 10 to 100 ppm. The blank, standards, and any dilutions should contain 2.5 ml of the aluminum solution and 50 ml of the sulfuric acid solution per 100 ml of solution.

#### Fuel Conditions

(see Molybdenum in Molybdenite.)

#### Remarks

*Application*-This procedure will determine the amount of  $\text{MoO}_3$  in ores and concentrates.

*Detection Limit*-The detection limit is about 0.005% molybdenum using a 2-g sample and the 10X expanded scale.

*Precision*-A relative deviation of  $\pm 5\%$  may be expected.

## SILVER IN ORES AND CONCENTRATES

Fire assay has been the accepted method for the determination of silver in ores for many years. Since atomic absorption is rapid and simple, much interest has been shown in applying this technique to silver determinations. In our laboratory, most reported methods have been of low precision, narrow application, or have yielded low results when compared with fire assay. The method listed below, however, gives good agreement with fire assay.

The distribution of silver in ores may not be homogeneous, therefore sample size is an important factor. The large sample size (15 to 30 g) used in fire assaying gives this method a definite advantage over atomic absorption. Nevertheless, with careful grinding, mixing, and quartering,

atomic absorption can give comparable results. The material should not be ground finer than -80 mesh however, because of the possibility of silver plating-out on the grinding surfaces.

Interference by silicate ions has been reported in the literature, but the author of the method reproduced below found no interference from silicate ions with the matrix he used.

#### Reagents

*Silver standard solution*, 1,000 ppm: Dissolve 1.574 g of silver nitrate ( $\text{AgNO}_3$ ) in distilled water and dilute to one liter with 1% (v/v) nitric acid. Store solution in an amber glass bottle.

*Ammonium hydroxide*, 58% (w/w): Concentrated, analytical grade.

#### Procedure

Weigh a 1.000- or 2.000-g sample into a 400-ml beaker.

Add 10 ml of hydrochloric acid, 5 ml of hydrofluoric acid, 10 ml of nitric acid and 5 ml of perchloric acid.

Evaporate the samples to dryness on a hotplate covering the samples with a watchglass for the first 30 minutes.

Cool. Add 5 ml of hydrochloric acid and 30 ml of distilled water (a portion of this water can be used to rinse any residue that remains on the watchglass into the beaker).

Warm the mixture for 5 minutes on a hotplate, then decant the liquid into a 100-ml volumetric flask.

Add 5 ml of perchloric acid to the residue in the beaker and evaporate to dryness.

Rinse the beaker and residue with 10 ml of distilled water, allow the solids to settle, and decant the liquid into the volumetric flask.

Rinse the beaker and residue with 30 ml of ammonium hydroxide, warm, allow the solids to settle, and decant the liquid into the volumetric flask.

Wash the beaker and residue with several portions of distilled water.

Cool the flask and contents to room temperature. Dilute to 100 ml with distilled water and mix.

Determine the silver by atomic absorption at 3281 Å using an oxidizing air-acetylene flame. Prepare standards in the range of 1 to 20 ppm. The blank, standards, and any dilutions should contain 5 ml of hydrochloric acid and 30 ml of ammonium hydroxide per 100 ml of solution.

#### Fuel Conditions

(same as for cobalt)

#### Remarks

*Application*—This method was specifically written for the determination of silver in ores and mineral products, particularly siliceous or sulfide ores. Silver halide minerals should be soluble in ammonium hydroxide, but no work has been done specifically on silver halides. Values obtained on these minerals should be checked against fire assay values.

We have used this method to determine silver in the range of 0.2 to 40 oz/ton. The values run the same or slightly higher than fire assay values.

*Detection Limit*—The detection limit for this method about 0.1 oz/ton using a 2-g sample and the 10X expanded scale.

*Precision*—A relative deviation of about  $\pm 2$  to 3% may be expected.

#### Reference

Walton, George, 1973, A method for the determination of silver in ores and mineral products by atomic absorption spectroscopy: *Analyst*, v. 98, p. 335-342.

### TIN IN ORES AND CONCENTRATES

Tin occurs in nature as the oxide, sulfide, and to a limited extent, as the native metal. The principal mineral is cassiterite,  $\text{SnO}_2$ . Cassiterite is only slightly acid soluble, so acid decomposition of tin ores is not recommended. Heating the sample with ammonium iodide and dissolving the resulting sublimed tin iodide in hydrochloric acid is a simple, rapid method of decomposing tin minerals. (See Application section for several exceptions.)

Tin in solution can easily be determined by atomic absorption in the nitrous oxide-acetylene flame. There is an enhancement effect of ammonium iodide on the absorption, but this can be nullified by adding the same amount of ammonium iodide to the blank and standards and any dilutions.

#### Reagents

*Tin standard solution*, 1,000 ppm: Dissolve 1.000 g of pure tin metal in 100 ml of concentrated hydrochloric acid and dilute to one liter with distilled water.

*10% Hydrochloric acid solution*, (v/v): Dilute 100 ml of concentrated hydrochloric acid to 1,000 ml with distilled water.

*Hydrochloric acid and ammonium iodide solution*: Dissolve 10 g of ammonium iodide ( $\text{NH}_4\text{I}$ ) in 100 ml of concentrated hydrochloric acid and dilute to 1,000 ml with distilled water.

## Procedure

1. Use 50- to 100-mg sample for concentrates, and 300- to 500-mg sample for ores.
2. Place the weighed sample in an 8-inch test tube, add 1 g of  $\text{NH}_4\text{I}$ , and mix thoroughly. Sprinkle a few grains of  $\text{NH}_4\text{I}$  on top of the mixture.
3. Carefully heat the test tube over an open flame. Be sure to heat only the end of the tube, so that the tin iodide ( $\text{SnI}_4$ ) will condense on the side of the tube. When  $\text{SnI}_4$  has ceased to be produced, allow the test tube to cool. For samples containing more than 30% tin, add another 1 g of  $\text{NH}_4\text{I}$  and heat again.
4. Add 10 ml of the hydrochloric acid solution. Heat the tube in a water bath to dissolve soluble salts.
5. Bring to volume in a 100-ml volumetric flask with the hydrochloric acid solution.
6. Prepare blank and standard solutions (25- 100 ppm) using the hydrochloric acid and ammonium iodide solution.
7. Determine tin by atomic absorption at 2863 Å using a reducing nitrous oxide-acetylene flame. (There are several tin lines available that can be used, depending on the amount of tin in the samples and the strength of your tin lamp. 2246 Å and 2706 Å are two of these lines.)
8. Adjust acetylene pressure to give the maximum "red feather" without the flame becoming luminous.
9. Rinse the aspirator, chamber, and burner with distilled water when finished.

## Fuel Conditions

Nitrous oxide: 30 psi; flowmeter, 5.0; 10.8 liters/minute.

Acetylene: 10 psi; flowmeter, 11.5; 6.0 liters/minute.

## Remarks

*Application*—This method applies specifically to the determination of tin in ores and concentrates. However, there are several very refractory varieties of cassiterite (stream tin, wood tin) which are not solubilized by the above procedure unless an acid pretreatment is used. The acid pretreatment removes iron minerals that evidently coat the cassiterite, preventing the formation of tin iodide. Weigh the sample into a 250-ml beaker, add 20 ml of hydrochloric acid and 2 ml of 30% hydrogen peroxide. Cover and digest for 30 minutes. Remove the cover and continue heating to reduce the volume by half. Add 50 ml of distilled water and filter through Whatman #42 filter paper. Place the filter paper in a porcelain crucible and burn off the filter paper. Quantitatively transfer the precipitate to an 8-inch test tube and proceed as indicated in step 2.

*Detection Limit*—The detection limit is about 0.05% tin using a 500-mg sample and the 10X expanded scale.

*Precision*—A relative deviation of  $\pm 5$  to 10% may be expected.

## Reference

Bowman, J. A., 1968, Determination of tin in tin ores and concentrates by atomic absorption spectrophotometry in the nitrous oxide-acetylene flame: *Anal. Chim. Acta*, v.42, p. 285-291.

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