

# Chemical Analysis of Barite

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# Chemical Analysis of Barite

## 1 Scope

**1.1** Barite is used to increase the density of oil well drilling fluids. It is a mined product that can contain significant quantities of minerals other than barium sulfate, which is its main component.

**1.2** A list of some minerals commonly associated with barite ores is given in Table 1 with the chemical formulas, mineralogical names, and the densities of the mineral grains.

**1.3** The performance of barite in a drilling fluid is related in part to the percentage and type of non-barite minerals distributed in the barite ore. Some of these minerals have little or no effect on drilling fluid properties, but others can degrade these properties and even be harmful to rig personnel.

**1.4** It is the objective of this publication to provide a comprehensive, detailed description of the chemical analytical procedures for quantitatively determining the mineral and chemical constituents of barite. These procedures are quite elaborate and will normally be performed in a well-equipped laboratory.

**Table 1—Minerals Associated with Barite Ore Bodies**

Mineral	Chemical Formula	Mineralogical Name	Relative Density	Hardness Mohs
Barium sulfate	BaSO <sub>4</sub>	Barite, barites, barytes	4.50	2.5–3.5
Strontium sulfate	SrSO <sub>4</sub>	Celestite	3.97	3.5
Barium carbonate	BaCO <sub>3</sub>	Witherite	4.30	3.5
Barium silicate	BaSi <sub>2</sub> O <sub>5</sub>	Sanbornite	3.74	5
Calcium carbonate	CaCO <sub>3</sub>	Calcite	2.72	3
Calcium magnesium carbonate	CaMg(CO <sub>3</sub> ) <sub>2</sub>	Dolomite	2.87	3.5–4
Magnesium carbonate	MgCO <sub>3</sub>	Magnesite	3.0	4
Calcium sulfate	CaSO <sub>4</sub> •2H <sub>2</sub> O	Gypsum	2.3	2
Calcium fluoride	CaF <sub>2</sub>	Fluorite	3.0	4
Iron (ferric) oxide	Fe <sub>2</sub> O <sub>3</sub>	Hematite	5.2	5.5
Iron oxyhydroxide	Fe <sub>2</sub> O <sub>3</sub> •nH <sub>2</sub> O	Goethite	3.3–4.0	5–5.5
Iron (II, III) oxide	Fe <sub>3</sub> O	Magnetite	5.16–5.17	5.5–6.5
Iron carbonate	FeCO <sub>3</sub>	Siderite	3.7–3.9	3.5–4
Iron sulfide	FeS <sub>2</sub>	Pyrite	5.0	6–6.5
Iron sulfide	Fe <sub>1-x</sub> S <sub>x</sub> (x=0 to 0.2)	Pyrrhotite	4.6	4
Iron/copper sulfide	CuFeS <sub>2</sub>	Chalcopyrite	4.2	4
Lead sulfide	PbS	Galena	7.5	2.5
Zinc sulfide	ZnS	Sphalerite	3.9	3.5–4
Ferrous titanate	FeTiO <sub>3</sub>	Ilmenite	4.7	5.5
Silicon dioxide	SiO <sub>2</sub>	Quartz, sand, chert	2.65	7
<b>Aluminosilicates:</b>				
Feldspar	(Na,K)AlSi <sub>3</sub> O <sub>8</sub>	Albite, microcline	2.6	6
Mica	KAl <sub>2</sub> (OH) <sub>2</sub> AlSi <sub>3</sub> O <sub>10</sub>	Muscovite	2.85	2.5
Clays	Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	Kaolinite	2.6	2
	(Al,Mg)(OH) <sub>2</sub> Si <sub>4</sub> O <sub>10</sub> (Na,Ca) <sub>x</sub> •4H <sub>2</sub> O	Montmorillonite	2–3	1–2

## 2 Normative References

The following referenced documents are indispensable for the application of this document. For dated references, on the edition cited applies. For undated references, the latest edition of the reference document (including any amendments) applies.

API 13B-1, *Field Testing Water-based Drilling Fluids*

ISO 3696, <sup>1</sup> *Water for analytical laboratory use—Specification and test methods*

## 3 Terms, Definitions, Acronyms, Abbreviations, and Symbols

### 3.1 Terms and Definitions

For the purposes of this document, the following terms and definitions apply.

#### 3.1.1

##### **ACS reagent grade**

Grade of chemical meeting the purity standards specified by the American Chemical Society <sup>2</sup> (ACS), with impurities measured in parts per million.

#### 3.1.2

##### **deionized water**

##### **distilled water**

Water for laboratory use of analysis of barite requiring high standard water that has meet or exceeded the purity of standards specified by ISO 3696 for water Grade III.

NOTE Determination of elements in trace quantities such as mercury, cadmium, and arsenic requires higher purity water Grade II.

#### 3.1.3

##### **spectral grade**

Grade of chemical exceeding the purity standards specified by the ACS, with impurities measured in parts per billion.

### 3.2 Acronyms and Abbreviations

For the purposes of this document, the following acronyms and abbreviations apply.

AA	atomic absorption (spectrophotometry)
ACS <sup>2</sup>	American Chemical Society
EPA <sup>3</sup>	U.S. Environmental Protection Agency
GGT	Garrett Gas Train
IC	ion chromatography
ICP <sup>4</sup>	inductively coupled plasma (spectrometry)

<sup>1</sup> International Organization for Standardization, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland; [www.iso.org](http://www.iso.org).

<sup>2</sup> American Chemical Society, 1155 Sixteenth Street, N.W., Washington, DC 20036, USA; [www.acs.org](http://www.acs.org).

<sup>3</sup> Environmental Protection Agency, 1200 Pennsylvania Avenue, N.W., Washington, DC 20460, USA; [www.epa.gov](http://www.epa.gov).

<sup>4</sup> This can be ICP-AES (inductively coupled plasma atomic emission spectrophotometer,) ICP-MS (inductively coupled plasma mass spectrophotometer), or an ICP-OES (inductively coupled plasma optical emission spectrophotometer).

NIST <sup>5</sup>	National Institute of Standards and Technology
OSPAR <sup>6</sup>	Convention for the Protection of the Marine Environment of the North–East Atlantic (Oslo-Paris)
PTFE	polytetrafluoroethylene
PVDC	polyvinylidene chloride
TC	to contain
TD	to deliver
UV	ultraviolet (spectrophotometer)
XRF	x-ray fluorescence

### 3.3 Symbols

For the purposes of this document, the following symbols apply.

$C_{As}$	arsenic mass concentration in barite sample, expressed in milligrams per kilogram
$C_{Cd}$	cadmium mass concentration in barite sample, expressed in milligrams per kilogram
$C_{Cl-aq}$	chloride mass concentration of water-soluble minerals, expressed in milligrams per kilogram
$C_{Cd-hydchlor\ ac}$	cadmium mass concentration in acid digested sample (HCl), expressed in micrograms per milliliter
$C_{CO_3}$	carbonate mass concentration in barite sample, expressed in milligrams per kilogram
$C_{CO_3-tot}$	total carbonate mass concentration (GGT procedure) in barite sample, expressed in milligrams per kilogram
$C_{Fe}$	iron mass concentration in extraction filtrate, expressed in milligrams per liter
$C_{Fe-aq\ reg}$	iron mass concentration by aqua regia extraction in barite sample, expressed in milligrams per kilogram
$C_{Fe-carb\ fus}$	iron mass concentration by carbonate fusion in barite sample, expressed in milligrams per kilogram
$C_{Fe-nitric\ ac}$	iron mass concentration by nitric acid extraction in barite sample, expressed in milligrams per kilogram
$C_{HCO_3}$	bicarbonate mass concentration in barite sample, expressed in milligrams per kilogram
$C_{Hg}$	mercury mass concentration of mercury in barite sample, expressed in milligrams per kilogram
$C_{Metal-aq}$	metal mass concentration of water-soluble minerals in barite sample, expressed in milligrams per kilogram
$C_{Metal-hydchlor\ ac}$	metal mass concentration of HCl-soluble minerals in barite sample, expressed in milligrams per kilogram
$C_{Metal-hydfleur,\ oxo\ ac}$	metal mass concentration of (HF-H <sub>2</sub> SO <sub>4</sub> -HN <sub>3</sub> -HClO <sub>4</sub> )-soluble minerals in barite sample, expressed in milligrams per kilogram

<sup>5</sup> National Institute of Standards and Technology, Gaithersburg, Maryland, USA; [www.nist.gov](http://www.nist.gov).

<sup>6</sup> OSPAR Commission, The Aspect, 12 Finsbury Square, London, EC2A 1AS, United Kingdom, [www.ospar.org](http://www.ospar.org).

$C_{OH}$	hydroxyl ion mass concentration in barite sample, expressed in milligrams per kilogram
$C_{Pb}$	lead mass concentration in barite sample, expressed in milligrams per kilogram
$C_{Pb-acetic\ ac}$	lead mass concentration in extraction filtrate (acetic acid), expressed in milligrams per liter
$C_{Pb-hydrochlor\ ac}$	lead mass concentration in acid digested sample (HCl), expressed in micrograms per milliliter
$C_{PO_4}$	phosphate mass concentration in barite sample, expressed in milligrams per kilogram
$C_S$	acid soluble sulfide mass concentration in barite sample, expressed in milligrams per kilogram
$C_{SO_4-aq}$	sulfate mass concentration of water-soluble minerals in barite sample, expressed in milligrams per kilogram
$C_{Zn-acetic\ ac}$	zinc mass concentration in extraction filtrate (acetic acid), expressed in milligrams per liter
$f_{Al_2O_3, \%}$	photometric correction factor for alumina, expressed as a percentage
$f_{CO_2}$	tube factor, i.e. 2.5 for Dräger tube CO <sub>2</sub> 100/a (cat No.8101811)
$f_S$	tube factor for sulfide detection, from Table 2
$f_{SiO_2, \%}$	photometric correction factor for silica, expressed as a percentage
$k$	percent barium sulfate correction factor taken from Figure 1, expressed as a percentage
$LOI$	loss on ignition in barite sample, expressed as a percentage
$l_{st}$	gas detection Dräger tube darkened length, expressed in units marked on the tube
$M_f$	volume of 0.01 mol/L (0.02N) H <sub>2</sub> SO <sub>4</sub> used in titration to reach methyl orange end point, expressed in milliliters
$m$	mass of the barite sample, expressed in grams
$m_{As}$	mass of arsenic in digested sample; expressed in micrograms
$m_{Hg}$	mass of mercury in digested sample; expressed in micrograms
$m_1$	mass of the precipitate, expressed in grams
$m_2$	mass of standard reference sample, expressed in grams
$m_3$	mass of the crucible, expressed in grams
$m_4$	mass of barite sample and crucible, expressed in grams
$m_5$	mass of ignited sample and crucible, expressed in grams
$n_1$	absorbance value for silica in standard reference sample, expressed in nanometers
$n_2$	absorbance value for silica in barite sample, expressed in nanometers
$n_3$	absorbance value for alumina in standard reference sample, expressed in nanometers
$n_4$	absorbance value for alumina in barite sample, expressed in nanometers
$P_f$	volume of 0.01 mol/L (0.02N) H <sub>2</sub> SO <sub>4</sub> used in titration to reach phenolphthalein end point, expressed in milliliters
$R$	AA or ICP reading value, expressed in milligrams per liter

$R_{IC}$	measured value from ion chromatograph, expressed in milligrams per liter
$R_M$	turbidimeter reading, expressed in milligrams per liter
$R_{PO_4}$	phosphate ion concentration reading from the calibration curve, expressed in milligrams per liter
$V$	volume of barite water-leachate filtrate sample used for titration, expressed in milliliters
$V_{AgNO_3}$	volume of silver nitrate used for titration, expressed in milliliters
$V_{HCl}$	volume of 0.1 mol/L (0.1N) HCl used in titration, expressed in milliliters
$V_o$	volume of digested solution, expressed in milliliters
$V_s$	volume of sample aliquot, expressed in milliliters
$V_{s,g}$	volume of sample added to generator, expressed in milliliters
$W_{Al_2O_3, \%}$	mass fraction of alumina minerals in barite sample, expressed as a percentage
$W_{Al_2O_3-Std, \%}$	alumina mass fraction of standard reference sample, expressed as a percentage
$W_{Al_2SiO_5, \%}$	aluminosilicates minerals mass fraction in barite sample, expressed as a percentage
$W_{As}$	mass fraction of arsenic in sample, expressed in milligrams per kilogram
$W_{BaO, \%}$	barium oxide mass fraction in barite sample, expressed as a percentage
$W_{BaSO_4, \%}$	barium sulfate mass fraction in barite sample, expressed as a percentage
$W_{BaSO_4-SrSO_4, \%}$	total mass concentration of barium and strontium sulfates in barite sample by co-precipitation, expressed as a percentage
$W_{CaCO_3, \%}$	calcium carbonate mass concentration in barite sample, expressed as a percentage
$W_{Ca(OH)_2, \%}$	calcium hydroxide (lime) mass fraction in barite sample, expressed as a percentage
$W_{Cmt, \%}$	cement mass fraction in barite sample, expressed as a percentage
$W_{Ca-aq, \%}$	calcium mass fraction of water-soluble minerals in barite sample, expressed as a percentage
$W_{Ca-hydchlor\ ac, \%}$	calcium mass fraction of HCl-soluble minerals in barite sample, expressed as a percentage
$W_{Elemt-barite, \%}$	element mass fraction in barite sample (as received), expressed as a percentage
$W_{Elemt-ash\ barite, \%}$	element mass fraction in ashed barite sample, expressed as a percentage
$W_{FeCO_3, \%}$	siderite (iron carbonate) mass fraction in barite sample, expressed as a percentage
$W_{Fe_2O_3, \%}$	hematite mass fraction in barite sample, expressed as a percentage
$W_{Fe_2S, \%}$	pyrite (iron sulfide) mass fraction in barite sample, expressed as a percentage
$W_{Gypsum, \%}$	gypsum mass fraction in barite sample, expressed as a percentage
$W_{PbCO_3, \%}$	lead carbonate mass fraction in barite sample, expressed as a percentage
$W_{Quartz, \%}$	mass fraction in barite sample, expressed as a percentage
$W_{SiO_2, \%}$	silica mass fraction in barite sample, expressed as a percentage
$W_{SiO_2-Std, \%}$	silica mass concentration of standard reference sample, expressed as a percentage

$W_{\text{Sr},\%}$	strontium mass fraction (AA or ICP) in barite sample, expressed as a percentage
$W_{\text{SrO},\%}$	strontium oxide mass fraction in barite sample, expressed as a percentage
$W_{\text{SrSO}_4,\%}$	strontium sulfate mass fraction in barite sample, expressed as a percentage
$W_{\text{ZnCO}_3,\%}$	zinc carbonate mass fraction in barite sample, expressed as a percentage

## 4 Wet Analysis Methods

### 4.1 Principle

**4.1.1** Classical wet chemical methods of analysis are commonly used to analyze barites. This is because the crystallographic technique of X-ray diffraction, used to determine individual crystalline mineral structures, does not work well with barite ores, due to the strong absorption of X-rays by barium atoms.

**4.1.2** These classical wet methods can determine the elements present in the sample but will not supply all the details of the association of elements to form specific minerals. Iron, for example, may be present as the oxide, carbonate, or sulfide, or be incorporated into the structure of a clay mineral. A few chemical analysis procedures are selective for certain minerals or compounds, but most of the mineral composition must be deduced from the total results of chemical analysis (see Annex A).

### 4.2 Advantages of Wet Chemical Analysis Methods

**4.2.1** If directions are carefully followed, most trained chemists or technicians can get good results within a reasonable time.

**4.2.2** The methods are selective, sensitive (usually in the parts per million [milligrams per liter or milligrams per kilogram] range), accurate, and reproducible (accuracy and reproducibility are usually 1 % or less).

**4.2.3** From the results of the wet analyses, one can usually determine approximate mineral or compound composition, or both.

**4.2.4** These methods have been thoroughly tested over a period of many years, most of them are the final test result of a long evolution of trial-and-error techniques.

### 4.3 Summary of General Analytical Methods

#### 4.3.1 Barium sulfate ( $\text{BaSO}_4$ )

Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) fusion, then gravimetric analysis.

#### 4.3.2 Strontium sulfate ( $\text{SrSO}_4$ )

Sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) fusion, then atomic absorption (AA) analysis or inductively coupled plasma (ICP).

#### 4.3.3 Silica ( $\text{SiO}_2$ ) and alumina ( $\text{Al}_2\text{O}_3$ )

Sodium hydroxide (NaOH) fusion, then colorimetric analysis.

#### 4.3.4 Sodium (Na) and potassium (K)

Hydrochloric acid (HCl) or hydrofluoric/sulfuric/nitric acid ( $\text{HF}/\text{H}_2\text{SO}_4/\text{HNO}_3$ ) extraction, or both, then flame emission analysis or ICP.

The only HCl insoluble Na and K compounds sometimes found in barite are Na and K feldspars, which are soluble in HF/H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> mixed acids. The difference in Na and K values obtained by these two extractions can give an estimate of Na and K feldspars in barite.

#### 4.3.5 Calcium (Ca), magnesium (Mg), and iron (Fe)

Hydrochloric acid (HCl) or hydrofluoric/sulfuric/nitric acid (HF/H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub>) extraction, or both, then AA or ICP analysis.

Following are compounds of Ca, Mg, or Fe sometimes found in barite, that are insoluble in HCl, but soluble in the HF/H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> mixture; the difference in Ca, Mg, and Fe values obtained by these two extractions can give estimates of these compounds in barite: fluorite (CaF<sub>2</sub>), talc (hydrous magnesium silicate), montmorillonite (Mg is usually present in lattice structure), and pyrite (FeS<sub>2</sub>).

#### 4.3.6 Alternative methods for iron (Fe)

Extraction with nitric (HNO<sub>3</sub>) or with hydrochloric/nitric (HCl/HNO<sub>3</sub>) acid, or fuse with carbonate, then determine by AA or ICP analysis.

#### 4.3.7 Copper (Cu), manganese (Mn), lead (Pb), and zinc (Zn)

Hydrochloric acid (HCl) extraction, then AA analysis.

#### 4.3.8 Siderite (FeCO<sub>3</sub>)

Ethylene diamine tetraacetic acid dihydrate (EDTA)/sodium hydroxide (NaOH) extraction, then AA or ICP analysis.

#### 4.3.9 Total carbonate (CO<sub>3</sub><sup>-2</sup>)

Determine by the Garrett Gas Train (GGT) method.

#### 4.3.10 Sulfide (S<sup>-</sup>)

Determined by the GGT method; alternative procedure—treat with 1 mol/L HCl or 0.5 mol/L H<sub>2</sub>SO<sub>4</sub>, analyze H<sub>2</sub>S evolved with lead acetate paper.

#### 4.3.11 Water soluble analysis

Barite is extracted with an equal weight of deionized water, and filtrate is analyzed for elements of interest by titration, AA, ICP, and flame emission techniques.

#### 4.3.12 Loss on ignition (LOI)

Weight loss after heating to 1000 °C (1830 °F), due to combined water lost from clays, decomposition of carbonates or organic and carbonaceous matter.

#### 4.3.13 Calcium hydroxide (lime) or cement content

Extract with an aqueous solution of sugar, and the lime/cement content titrated with standardized HCl solution.

## 5 Barium Sulfate and Strontium Sulfate

### 5.1 Principle

This procedure determines barium sulfate (BaSO<sub>4</sub>) and strontium sulfate (SrSO<sub>4</sub>) in barites by fusion with sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), dissolution with hydrochloric acid (HCl) and measurement of barium (Ba) gravimetrically

by sulfate precipitation and, of strontium (Sr) by atomic absorption (AA) or inductively coupled plasma (ICP) analysis.

## 5.2 Reagents and Materials

**WARNING** Concentrated acids (hydrochloric or sulfuric) are strong, potentially harmful acids. Use proper safety precautions when handling them.

**5.2.1 Deionized or distilled water** shall be in accordance with ISO 3696 of at least Grade III.

Use deionized or distilled water for preparation of all reagents and calibration standards and as dilution water.

**5.2.2 Sodium carbonate** ( $\text{Na}_2\text{CO}_3$ ) (CAS No. 497-19-8), anhydrous, ACS grade powder.

**5.2.3 Sodium carbonate solution** (0.2 % w/w), 1.0 g  $\text{Na}_2\text{CO}_3$  dissolved in 500 mL deionized water.

**5.2.4 Hydrochloric acid solution 6 mol/L (6N)** (CAS No. 7647-01-0), ACS reagent grade.

**5.2.5 Sulfuric acid solution 10 % w/w** (CAS No. 7664-93-9), ACS reagent grade.

**5.2.6 Sulfuric acid solution 1 % by volume** (CAS No. 7664-93-9), ACS reagent grade.

**5.2.7 Strontium AA or ICP standards**, 5 mg/L, 10 mg/L, and 15 mg/L Sr in 1 % w/w HCl.

**5.2.8 Ammonium hydroxide** (CAS No. 1336-21-6),  $\text{NH}_4\text{OH}$ , concentrated (28 % to 30 %), ACS reagent grade.

**5.2.9 Methyl orange indicator solution** (CAS No. 547-58-0), 0.1 g methyl orange diluted to 100 mL with deionized water.

## 5.3 Apparatus

**5.3.1 Mortar and pestle.**

**5.3.2 Sieve**, 150  $\mu\text{m}$  (0.0059 in.-U.S. sieve No.100).

**5.3.3 AA or ICP spectrophotometer**, any AA or ICP unit is suitable. Instrument settings recommended by the manufacturer should be followed.

**5.3.4 Analytical balance**, with accuracy of 0.001 g (1 mg).

**5.3.5 Stirring rod, glass, or polytetrafluoroethylene (PTFE)** equivalent plastic, one end fitted with a rubber policeman.

**5.3.6 Crucibles and lids**, platinum, two 25 mL.

**5.3.7 Crucible tongs**, one 25 cm (10 in.) or one 50 cm (20 in.).

**5.3.8 Muffle furnace**, regulated to 1000 °C  $\pm$ 20 °C (1830 °F  $\pm$ 35 °F).

**5.3.9 Beakers**, four 250 mL, two 400 mL, and two 600 mL.

**5.3.10 Watch glasses**, two fitted for 250 mL beaker and two fitted for 600 mL beaker.

**5.3.11 Hot plate.**

**5.3.12 Funnels**, glass, two, 65 mm (2.5 in.) long stem.

**5.3.13 Filter paper**, grade 40<sup>7</sup> or equivalent, quantitative, ashless, medium filtration rate, circle 110 mm.

**5.3.14 Filter paper**, grade 541<sup>8</sup> or equivalent, quantitative, hardened, ash-less, fast filtration rate, circle 110 mm.

**5.3.15 Volumetric flasks**, to contain (TC), two, 250 mL.

**5.3.16 Annealing cups**, two, typical capacity 15 mL (diameter 35 mm, height 25 mm).

**5.3.17 Desiccator**.

**5.3.18 Volumetric pipette**, to deliver (TD), one 10 mL.

**5.3.19 Medicine droppers**, two.

## 5.4 Sampling

Use a representative sample ground such that 100 % passes through the 150  $\mu\text{m}$  sieve (see 5.3.2).

## 5.5 Procedure—Barium Sulfate Determination

The following procedure shall be applied to determine barium sulfate mass concentration.

- a) Accurately weigh a 1.0 g representative barite sample to 0.001 g (1 mg). Record sample mass, expressed in g, as  $m$ .

NOTE It is advisable to perform this analysis in duplicate. If this is done, a slightly smaller sample, e.g. 0.80 g to 0.001 g (1 mg), of barite may be used to check accuracy and precision of this procedure.

- b) Transfer sample to a 25 mL platinum crucible containing 6.0 g  $\pm 0.1$  g  $\text{Na}_2\text{CO}_3$ . Mix thoroughly with stirring rod. Cover the mixture with an additional 2.0 g  $\pm 0.1$  g  $\text{Na}_2\text{CO}_3$ .
- c) Fuse for 1 h at 1000 °C (1830 °F) in the muffle furnace. Have a crucible lid on crucible during fusion.

NOTE When beginning the fusion, the furnace may be hot or cold.

- d) Remove from furnace with crucible tongs and while contents are still molten, give a slow rotary motion so that melt will spread over the sides and solidify as a thin shell over the interior. This procedure later facilitates the removal of the contents.

**WARNING Use proper safety precautions while handling hot crucible and melt.**

- e) Allow to cool. Place crucible and lid in a 250 mL beaker containing 150 mL deionized water. Digest on warm hot plate until melt has completely disintegrated and can easily be removed from crucible.

NOTE Digesting overnight is preferable.

- f) Remove the crucible from beaker with rubber policeman and wash inside and out with distilled water. Remove crucible lid and wash also.

<sup>7</sup> This grade 40 filter paper is a calendared, hardened, quantitative, ashless filter paper made from high-quality cotton linters designed for medium filtration rate and retention. The filter paper has the following typical properties which may vary by manufacturer: filtration rate: 340 s/100 mL (Herzberg method); particle retention: 8  $\mu\text{m}$  (at 98 % efficiency); ash content <0.007 % by weight; basis weight: 95 g/m<sup>2</sup> (0.019 lb/ft<sup>2</sup>); thickness: 0.210 mm (0.008 in.).

<sup>8</sup> This grade 541 filter paper is a calendared, hardened, quantitative, ashless filter paper made from high-quality cotton linters designed for fast filtration rate and coarse retention of particles or gelatinous precipitates. The filter paper has the following typical properties which may vary by manufacturer: filtration rate: 34 s/100 mL (Herzberg method); particle retention: 22  $\mu\text{m}$  (at 98 % efficiency); ash content <0.006 % by weight; basis weight: 82 g/m<sup>2</sup> (0.017 lb/ft<sup>2</sup>); thickness: 0.155 mm (0.0061 in.).

- g) Filter through grade 40 filter paper (see 5.3.13), transferring all solids to filter paper. Wash filter paper and solids 12 times with hot 0.2 %  $\text{Na}_2\text{CO}_3$  solution. Discard filtrate.

NOTE If iron content (see Section 8 or Section 9) is less than 5 %, proceed to Item i). If iron content is more than 5 %, then precipitation of iron hydroxide along with barium sulfate can cause an error. In this case, go to Item h), which gives a method for removing iron and aluminum.

- h) Use the following method for removing iron and aluminum from barite:

- 1) Dissolve the carbonates with hot 6 mol/L HCl, catching the solution in a 250 mL beaker. The funnel must be covered with a watch glass while adding the acid dropwise with a medicine dropper. Raise the watch glass just enough to insert the dropper.

NOTE If strontium is to be run, catch solution in a 250 mL volumetric flask and dilute to volume mark. With a dry pipette, remove a 10 mL aliquot for strontium and transfer remaining volume into a 400 mL beaker.

- 2) Remove iron and aluminum by addition  $\text{NH}_4\text{OH}$  dropwise until fumes of ammonia ( $\text{NH}_3$ ) are given off.
- 3) Filter through grade 541 filter paper (see 5.3.14), catching the filtrate in a 600 mL beaker.
- 4) Redissolve the precipitate with 6 mol/L HCl, catching the filtrate in a 250 mL beaker.
- 5) Reprecipitate the iron and aluminum with  $\text{NH}_4\text{OH}$  and filter into a 600 mL beaker from Item 3).
- 6) Bring the filtrate to ~400 mL. Add a few drops of methyl orange and titrate with 6 mol/L (6N) HCl. Add 1 mL excess 6 mol/L HCl. Filtrate should now be at the correct pH to precipitate the  $\text{BaSO}_4$  according to Item m) through Item p).

- i) Dissolve the carbonates [barium (Ba), strontium (Sr), chromium (Cr)] from the paper with warm 6 mol/L HCl solution catching the solution in a 600 mL beaker. The funnel must be covered with a watch glass while adding the acid dropwise with a medicine dropper. Raise the watch glass just enough to insert the dropper.

NOTE If strontium is to be run, catch solution in a 250 mL volumetric flask, wash the filter paper and dilute to volume mark. With a dry pipette, remove a 10 mL aliquot for strontium and transfer remaining volume into a 600 mL beaker for barium analysis.

- j) After carbonates are dissolved, rinse the crucible and lid with warm 6 mol/L HCl and pour through filter paper.

NOTE There may be a few solids undissolved, such as iron oxide, which may be disregarded.

- k) Wash paper thoroughly with deionized water.

- l) Dilute filtrate to ~400 mL and boil using stirring rod instead of boiling chips.

- m) To the boiling solution, add 10 mL  $\text{H}_2\text{SO}_4$  10 % solution (see 5.2.6) dropwise and boil for 15 min. Allow to stand for at least 4 h. Keep hot but do not boil.

- n) Filter through grade 40 filter paper (see 5.3.13), transferring all of precipitate to filter paper. Wash 6 times with 1 %  $\text{H}_2\text{SO}_4$  solution, draining out the filtrate completely after each wash.

- o) Place filter paper in a tared annealing cup. Heat slowly from cold to 850 °C (1560 °F) in the muffle furnace and hold at that temperature for 1 h.

NOTE The  $\text{BaSO}_4$  precipitate should be white.

- p) Remove from furnace, and cool to room temperature in desiccator. Reweigh the  $\text{BaSO}_4$  precipitate and annealing cup on the analytical balance to the nearest 0.001 g. Record precipitate mass as  $m_1$ .

## 5.6 Procedure—Strontium Sulfate Determination

To determine strontium mass fraction expressed as a percentage,  $w_{\text{Sr},\%}$ , the 10 mL aliquot taken in 5.5 Item i) for Sr shall be analyzed on an AA spectrophotometer or an ICP spectrometer using prepared standards for Sr and manufacturer's recommendations for AA or ICP instrument settings.

## 5.7 Calculation—Barium Sulfate and Strontium Sulfate Mass Fractions

### 5.7.1 Barium Sulfate, No Strontium

If no strontium is present, the mass fraction of barium sulfate,  $w_{\text{BaSO}_4,\%}$ , in barite sample expressed as a percentage, shall be given in Equation (1).

$$w_{\text{BaSO}_4,\%} = 100 \times \left( \frac{m_1}{m} \right) \quad (1)$$

where

$m$  is the mass of the barite sample, expressed in grams;

$m_1$  is the mass of the precipitate, expressed in grams.

NOTE If a 10 mL aliquot was taken for Sr determination, use in Equation (1) 104.17 coefficient rather than 100.

### 5.7.2 Barium and Strontium Sulfates

If strontium is present, the total mass fraction in barite sample of barium and strontium sulfates,  $w_{\text{BaSO}_4-\text{SrSO}_4,\%}$ , that are co-precipitated, expressed as a percentage shall be given in Equation (2).

$$w_{\text{BaSO}_4-\text{SrSO}_4,\%} = 100 \times \left( \frac{m_1}{m} \right) \quad (2)$$

where

$m$  is the mass of the barite sample, expressed in grams;

$m_1$  is the mass of the precipitate, expressed in grams.

NOTE If a 10 mL aliquot was taken for Sr determination use in Equation (2) 104.17 coefficient rather than 100.

Then, strontium sulfate mass fraction,  $w_{\text{SrSO}_4,\%}$ , in barite sample, expressed as a percentage, shall be calculated by Equation (3) which is based on strontium mass fraction determined in 5.6 from AA spectrophotometry or ICP spectrometry.

$$w_{\text{SrSO}_4,\%} = 2.0963 \times w_{\text{Sr},\%} \quad (3)$$

where

$w_{\text{Sr},\%}$  is the mass fraction of strontium from AA or ICP (see 5.6), expressed as a percentage.

This amount of  $\text{SrSO}_4$  shall be used to obtain barium sulfate correction factor  $k$ , used in Equation (4) from the correction curve in Figure 1.

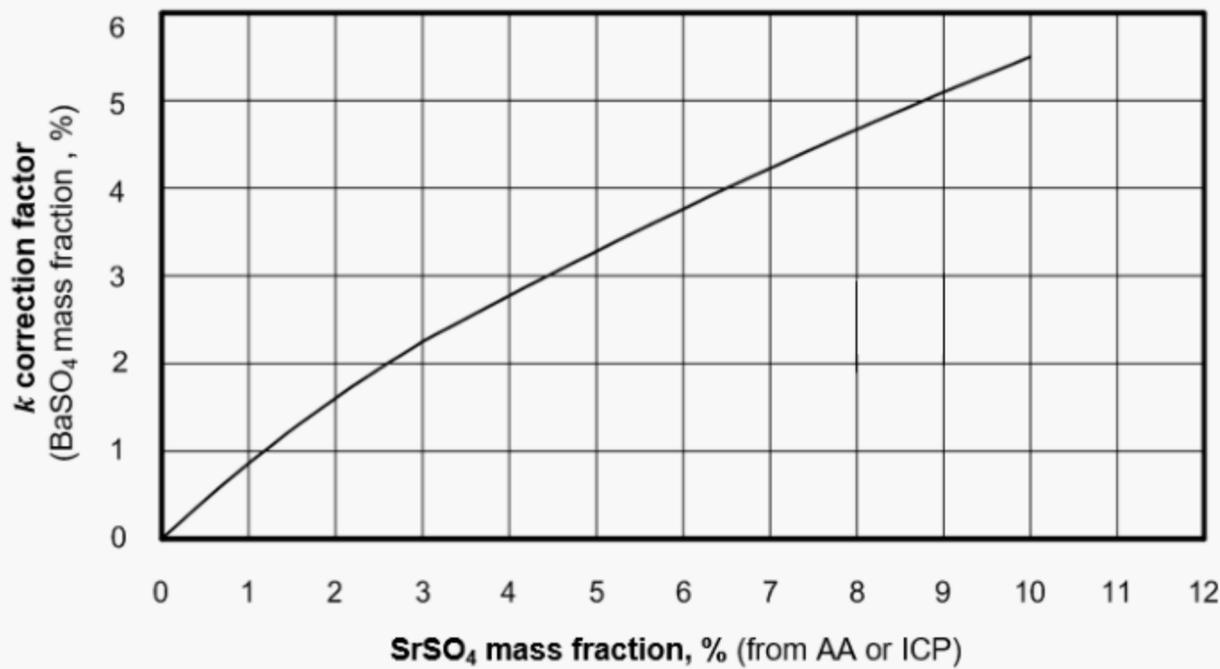


Figure 1—Typical Correction Curve for SrSO<sub>4</sub> in BaSO<sub>4</sub>

Barium sulfate mass fraction,  $w_{\text{BaSO}_4, \%}$ , in barite sample, expressed as a percentage shall be given in Equation (4).

$$w_{\text{BaSO}_4, \%} = \left[ w_{\text{BaSO}_4 - \text{SrSO}_4, \%} \right] - k \quad (4)$$

where

$w_{\text{BaSO}_4 - \text{SrSO}_4, \%}$  is the total mass concentration of barium sulfate and strontium sulfates determined by co-precipitation [Equation (2)], expressed as a percentage;

$k$  is the percentage barium sulfate correction factor taken from Figure 1.

## 6 Silica and Alumina

### 6.1 Principle

Silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>) occur in barite ores mostly as aluminosilicates (e.g. clays, feldspars, micas, and other minerals) and quartz. These two oxides are determined by fusing the barite with NaOH and then measuring the Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> by colorimetric analysis.

### 6.2 Reagents and Materials

**WARNING** Concentrated acids (hydrochloric or sulfuric) are strong, potentially harmful acids. Use proper safety precautions when handling them.

**6.2.1 Deionized or distilled water** shall be in accordance with ISO 3696 of at least Grade III.

Use deionized or distilled water for preparation of all reagents and calibration standards and as dilution water.

**6.2.2 Sulfuric acid solution, 20 % w/w** (CAS No. 7664-93-9), ACS reagent grade.

**6.2.3 Hydrochloric acid solution, 6 mol/L (6N)** (CAS No. 7647-01-0), ACS reagent grade.

**6.2.4 Ammonium molybdate solution** (CAS No. 12027-67-7), ACS reagent grade; 7.5 g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>•4H<sub>2</sub>O dissolved in 75 mL deionized water and 25 mL 20 % w/w H<sub>2</sub>SO<sub>4</sub>, stored in plastic bottle.

**6.2.5 Tartaric acid solution, 10 % w/w solution** (CAS No. 87-69-4) ACS reagent grade; 50 g tartaric acid dissolved in 450 mL deionized water, store in plastic bottle.

### 6.2.6 Reducing solution

Dissolve 0.7 g sodium sulfite (CAS No. 7757-83-7) in 10 mL deionized water. Add 0.15 g 1-amino-2-naphthol-4-sulfonic acid (CAS No. 90-51-7) and stir until dissolved. Dissolve 9 g sodium bisulfite (CAS No. 7631-90-5) in 90 mL deionized water. Add this solution to the first solution, and mix.

NOTE This solution is not stable and should be prepared fresh just prior to use.

**6.2.7 Hydroxylamine hydrochloride 10 % solution** (CAS No. 5470-11-1). Dissolve 50 g of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) in 450 mL deionized water.

**6.2.8 Calcium chloride solution** (CAS No. 10043-85-4).

Transfer 7 g  $\text{CaCO}_3$  to a 250 mL beaker, add 100 mL water and 15 mL concentrated HCl 37 % w/w. Heat to boiling and boil for a few minutes. Cool to room temperature and pour into 500 mL volumetric flask. Dilute to 500 mL mark.

**6.2.9 Potassium ferricyanide solution (0.75 %)** (CAS No. 13746-66-2), add 0.375 g  $\text{K}_3\text{Fe}(\text{CN})_6$  to 50 mL deionized water just before using.

**WARNING** Potassium ferricyanide is toxic through inhalation, ingestion, or skin contact; avoid contact or any chance of ingestion.

**CAUTION** Do not store the potassium ferricyanide solution.

**6.2.10 Buffer solution**, 100 g sodium acetate (CAS No. 127-09-3), dissolve  $\text{NaC}_2\text{H}_3\text{O}_2\cdot\text{H}_2\text{O}$  in 200 mL deionized water, add 30 mL glacial acetic acid (CAS No. 64-19-7) and dilute to 500 mL with deionized water.

**WARNING** Avoid skin contact with glacial acetic acid.

**6.2.11 Alizarin Red S solution (0.05 %)** (sodium alizarine sulfonate) (CAS No. 130-22-3), add 0.25 g Alizarin Red S to 500 mL deionized water, stirred and filtered.

**6.2.12 Thioglycolic acid (mercaptoacetic acid) solution 4 %** (CAS No. 68-11-1), add 4.0 g  $\text{HSCH}_2\text{COOH}$  to 96 mL deionized water just before using.

NOTE Do not store the solution to avoid oxidation.

**6.2.13 Sodium hydroxide solution (30 %)** (CAS No. 1310-73-2), dissolve 30.0 g NaOH in 70 mL deionized water, stored in plastic bottle.

**6.2.14 NIST Standard Reference Materials 70b (potassium feldspar)**, or equivalent standard reference.

## 6.3 Apparatus

**6.3.1 Ultraviolet (UV)/visible spectrophotometer**, any UV/visible spectrophotometer with photometric precision of 0.001 absorbance is suitable.

**6.3.2 UV cells**, 1 cm, glass, or quartz.

**6.3.3 Graduated cylinder**, plastic, one 10 mL.

**6.3.4 Crucibles and lids**, nickel, several 75 mL.

**6.3.5 Hot plate**.

**6.3.6 Analytical balance**, with accuracy of 0.001 g (1 mg).

6.3.7 **Bunsen burner**, tripod, and triangle.

6.3.8 **Stirring rods**, PTFE or equivalent.

6.3.9 **Beakers**, glass, four or more 600 mL.

6.3.10 **Volumetric flasks** (TC), one 1000 mL, one 500 mL and one 100 mL.

6.3.11 **Volumetric pipettes** (TD), one 1 mL, one 2 mL, one 5 mL, and one 10 mL.

6.3.12 **Serological pipettes** (TD), one 1 mL, one 2 mL, one 5 mL, and one 10 mL.

6.3.13 **Graduated cylinder** (TC), glass, one 10 mL.

6.3.14 **Filter paper**, quantitative, ashless, medium filtration rate, grade 40 (see 5.3.13) or grade 42<sup>9</sup> or equivalent, circle 110 mm.

#### 6.4 Procedure—Sample Preparation

The following procedure shall be applied to prepare samples (blank, standard reference, and barite sample).

- a) Clean each nickel crucible with dilute HCl prior to use.
- b) Transfer 5 mL portions of 30 % NaOH solution measured with a plastic graduated cylinder to a series of 75 mL nickel crucibles. One crucible will be needed for each sample, one for barite sample, one for standard reference material, and another one for blank.
- c) Evaporate the NaOH solution of each crucible to dryness on a hot plate.
- d) Accurately weigh a 0.10 g to 0.15 g representative barite sample to 0.001 g. Record sample mass expressed in g, as  $m_1$ . Transfer to a crucible containing NaOH. Use 50 mL portions of NaOH solution 30 %.

Weigh a 0.10 g to 0.15 g sample of standard reference material to 0.001 g. Record standard reference mass expressed in g, as  $m_2$ . Transfer to a crucible containing NaOH. Use 50 mL portions of NaOH solution 30 %.

NOTE A blank is prepared with 50 mL portion of NaOH solution 30 %.

- e) Cover and heat the crucibles over Bunsen burner to a dull redness for ~5 min. Remove each crucible from the heat and swirl the melt around the sides. Allow melt to cool.

**WARNING** The hot melt is potentially harmful, use good laboratory practices (safety precautions) while working with it.

- f) Add 50 mL of deionized water to each crucible, cover, and allow crucible to stand until melt disintegrates completely. Time can vary from one hour, if solutions are stirred occasionally, to overnight.
- g) Rinse each 600 mL beaker with 6 mol/L HCl. Place in each beaker an acid solution of 400 mL deionized water and 20 mL of 6 mol/L HCl.
- h) Transfer the contents of each crucible to a 600 mL beaker prepared item g) (i.e. barite sample, standard reference material, and blank). PTFE stirring rod should be used and care shall be taken so that the alkaline

<sup>9</sup> This grade 42 filter paper is a calendared, quantitative, ash-less filter paper made from high-quality cotton linters, designed for medium to slow filtration rate and finest particle retention. The filter paper has the following typical properties which may vary by manufacturer: filtration rate: 1870 s/100 mL (Herzberg method); particle retention): 2.5  $\mu\text{m}$  (at 98 % efficiency); ash content <0.007 % by weight; basis weight: 100 g/m<sup>2</sup> (0.020 lb/ft<sup>2</sup>); thickness: 0.200 mm (0.0079 in.).

solutions will not contact the side of the beaker but drain directly into the acid solution. Scrub and wash each crucible.

- i) Transfer contents of each beaker to a 1000 mL volumetric flask and dilute to mark with deionized water. The solutions containing barite and reference standard material will be cloudy.
- j) Centrifuge a 40 mL to 50 mL portion of each solution to obtain clear solution for  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  analyses, or alternatively, allow sample to settle and pipette aliquots from top of sample.

NOTE If solutions are not to be used the same day, transfer to tightly stoppered plastic bottle for storage, to avoid evaporation and possible contamination with silica from the glass flask.

### 6.5 Procedure—Silica Determination

The following procedure shall be applied to determine silica concentration.

- a) Rinse a 100 mL volumetric flask for each sample prepared in 6.4 Item j) with 6 mol/L HCl followed by deionized water before using.
- b) Transfer 10 mL of each sample solution (i.e. barite sample, standard reference, and blank solution) prepared in 6.4 Item j) to volumetric flasks. Add ~50 mL deionized water to each flask.
- c) Add 2 mL ammonium molybdate solution with a pipette. Swirl the flask during the addition. Allow to stand for 10 min.
- d) Add 4 mL tartaric acid solution with a pipette to each flask and swirl the flask while adding.
- e) Add 1 mL reducing solution with a pipette to each flask and swirl the flask while adding.
- f) Dilute each flask to volume mark (100 mL) with deionized water. Mix well and allow to stand for at least 30 min. Fresh reducing solution should be used each time the test is run.
- g) Determine the absorbance for standard reference material solution and barite sample solution at 640 nm. Use the reagent blank solution as the “zero” reference. Record the value for each solution, as  $n_1$  for the standard reference sample and  $n_2$  for the barite sample.

### 6.6 Procedure—Alumina Determination

The following procedure shall be applied to determine alumina concentration.

- a) Transfer 15 mL of each solution prepared in 6.4 Item j) (i.e. barite sample, standard reference, and blank) to 100 mL volumetric flasks.
- b) Add 2 mL calcium chloride solution to each flask.
- c) Add 1 mL 10 % hydroxylamine hydrochloride solution to each flask and swirl to mix.
- d) Add 1 mL potassium ferricyanide solution to each flask and swirl to mix.
- e) Add 2 mL thioglycolic acid solution to each flask and mix. Allow to stand 5 min.
- f) Add 10 mL Alizarin Red S solution with a pipette to each flask.
- g) Dilute to each flask volume mark (100 mL) with deionized water. Mix and allow to stand 1 h  $\pm$  15 min.

- h) Determine the absorbance at 475 nm for each solution. Use the reagent blank solution as the “zero” reference. Record the value for each solution, as  $n_3$  for the standard sample and  $n_4$  for the barite sample.

## 6.7 Calculation—Silica and Alumina Mass Fractions

### 6.7.1 Silica Mass Fraction

**6.7.1.1** The photometric correction factor for silica,  $f_{\text{SiO}_2, \%}$ , expressed as a percentage, knowing the silica mass fraction of the standard reference sample shall be given Equation (5).

$$f_{\text{SiO}_2, \%} = w_{\text{SiO}_2\text{-Std}, \%} \times \left( \frac{m_2}{n_1} \right) \quad (5)$$

where

$w_{\text{SiO}_2\text{-Std}, \%}$  is the silica mass fraction of the standard reference sample, expressed as a percentage;

$m_2$  is the mass of standard reference sample, expressed in grams;

$n_1$  is the absorbance value for silica in standard sample, expressed in nanometers.

**6.7.1.2** The silica mass fraction of the barite sample,  $w_{\text{SiO}_2, \%}$ , expressed as a percentage, shall be given in Equation (6).

$$w_{\text{SiO}_2, \%} = f_{\text{SiO}_2, \%} \times \left( \frac{n_2}{m} \right) \quad (6)$$

where

$f_{\text{SiO}_2, \%}$  is the photometric correction factor for silica, expressed as a percentage;

$m$  is the mass of the barite sample, expressed in grams;

$n_2$  is the absorbance value for silica in barite sample, expressed in nanometers.

### 6.7.2 Alumina Mass Fraction

**6.7.2.1** The photometric correction factor for alumina,  $f_{\text{Al}_2\text{O}_3, \%}$ , expressed as a percentage, knowing the alumina mass fraction of the standard reference sample, shall be given in Equation (7).

$$f_{\text{Al}_2\text{O}_3, \%} = w_{\text{Al}_2\text{O}_3\text{-Std}, \%} \times \left( \frac{m_2}{n_3} \right) \quad (7)$$

where

$w_{\text{Al}_2\text{O}_3\text{-Std}, \%}$  is the alumina mass fraction of the standard reference sample, expressed as a percentage;

$m_2$  is the mass of standard reference sample, expressed in grams;

$n_3$  is the absorbance value for alumina in standard sample, expressed in nanometers.

**6.7.2.2** The alumina mass fraction of the barite sample,  $w_{\text{Al}_2\text{O}_3, \%}$ , expressed as a percentage, shall be given in Equation (8).

$$w_{\text{Al}_2\text{O}_3, \%} = f_{\text{Al}_2\text{O}_3, \%} \times \left( \frac{n_4}{m} \right) \quad (8)$$

where

- $f_{\text{Al}_2\text{O}_3, \%}$  is the photometric correction factor for alumina concentration, expressed as a percentage;
- $m$  is the mass of the barite sample, expressed in grams;
- $n_4$  is the absorbance value for alumina in barite sample, expressed in nanometers.

## 7 Hydrochloric Acid Soluble Metals—Sodium, Potassium, Calcium, Magnesium, Iron, Copper, Manganese, Lead, and Zinc

### 7.1 Principle

**7.1.1** The hydrochloric acid soluble metals usually analyzed in barite are sodium, potassium, calcium, magnesium, iron, copper, manganese, lead, and zinc. Most of the compounds of these metals found in barite are soluble under the conditions of this test.

**7.1.2** Exceptions to acid solubility are pyrite ( $\text{FeS}_2$ ) and sodium feldspars and potassium feldspars. Fluorite ( $\text{CaF}_2$ ) slowly dissolves but may not be completely dissolved during the digestion time called for in the procedure. The magnesium in montmorillonite and talc is also not analyzed by this procedure. For a total analysis of these metals, see Section 8.

### 7.2 Reagents and Materials

**WARNING** Concentrated acids (hydrochloric or nitric) are strong, potentially harmful acids. Use proper safety precautions when handling them.

**7.2.1 Deionized or distilled water** shall be in accordance with ISO 3696 of at least Grade III.

Use deionized or distilled water for preparation of all reagents and calibration standards and as dilution water.

**7.2.2 Hydrochloric acid concentrated** (CAS No. 7647-01-0), 37 % w/w, ACS reagent grade.

**7.2.3 Hydrochloric acid solution 1 %** (CAS No. 7647-01-0).

**7.2.4 Nitric acid solution 1 %** (CAS No. 7697-37-2).

**7.2.5 AA or ICP standards**, prepared in 1 % HCl.

**NOTE** Potential matrix interferences are seen for some metals when using HCl and ICP may be avoided by substituting 1 % HCl to 1 %  $\text{HNO}_3$ .

### 7.3 Apparatus

**7.3.1 Sieve**, 150  $\mu\text{m}$  (0.0059 in.-U.S. sieve No. 100).

**7.3.2 AA spectrophotometer or ICP spectrometer**, any AA or ICP unit is suitable. Instrument settings recommended by the manufacturer should be followed.

**7.3.3 Analytical balance**, with accuracy of 0.001 g (1 mg).

**7.3.4 Graduated cylinder** (TD), one 25 mL.

**7.3.5 Beakers**, glass, ten 250 mL.

**7.3.6 Hotplate stirrer**.

### 7.3.7 Stirring bar.

### 7.3.8 Watch glasses, to cover 250 mL beakers.

## 7.4 Procedure

To determine hydrochloric acid soluble metal concentrations in barite sample, the following procedure shall be applied:

- a) Use a representative sample of barite ground such that 100 % passes through sieve (see 7.3.1).
- b) Accurately weigh a 1.0 g to 1.5 g representative sample of barite to 0.001 g (1 mg) into a 250 mL beaker. Record sample mass expressed in g, as  $m$ .
- c) Add 20 mL concentrated HCl. Place a magnetic stirring bar into beaker, and cover with a watch glass.
- d) Boil while stirring for 30 min. Add water as necessary during this period to maintain 20 mL volume.
- e) Cool and transfer to a 100 mL volumetric flask.
- f) Dilute to volume mark (100 mL) with deionized water.
- g) Allow solids to settle. If solids do not settle, filter, or centrifuge the sample.
- h) Analyze the clear supernatant using an AA or ICP spectrophotometer. Run the standards prepared in 1 % HCl or 1 % HNO<sub>3</sub> solution. Record all values for the supernatant and standard solutions.

## 7.5 Calculation

The mass concentration of each metal shall be calculated by multiplying the results obtained on the AA or ICP spectrophotometer by the correction factor for the analyzed volume used (here 100/1000 = 1/10), and for weight of barite sample (1000/ $m$ ).

Metal mass concentration in barite sample, soluble in HCl,  $c_{\text{Metal-hydrochlor ac}}$ , expressed in milligrams per kilogram shall be given in Equation (9).

$$c_{\text{Metal-hydrochlor ac}} = 100 \times \left( \frac{R}{m} \right) \quad (9)$$

where

$R$  is the AA or ICP reading value, expressed in milligrams per liter;

$m$  is the mass of the barite sample, expressed in grams.

## 8 Procedure—Hydrofluoric, Sulfuric, Nitric, Perchloric Acid Soluble Metals—Sodium, Potassium, Calcium, Magnesium, Iron, Copper, Manganese, Lead, and Zinc

### 8.1 Principle

The hydrofluoric, sulfuric, nitric, perchloric acid soluble metals are sodium, potassium, calcium, magnesium, iron, copper, manganese, lead, and zinc. This acid extraction dissolves minerals in barite that contain these metals, including pyrite, feldspars, fluorite, talc, and clays. By comparing the result of this analysis to the results of the hydrochloric acid soluble metals (see Section 7), an approximation of the pyrite, feldspars, etc. in the barite sample may be made (see Annex A).

## 8.2 Reagents and Materials

**WARNING** Strong acids and toxic mixture are required. Use all proper safety precautions when handling them. Avoid skin contact, wear protective clothing and eye/face protection and work under a fume hood.

**8.2.1 Deionized or distilled water** shall be in accordance with ISO 3696 of at least Grade III.

Use deionized or distilled water for preparation of all reagents and calibration standards and as dilution water.

**8.2.2 Nitric acid concentrated** (CAS No. 7697-37-2) (70 % w/w), ACS reagent grade.

**WARNING** Concentrated nitric acid is a strong, potentially harmful acid. Use proper safety precautions when handling it.

**8.2.3 Hydrochloric acid solution 1 %** (CAS No. 7647-01-0), ACS reagent grade.

**8.2.4 Nitric acid solution 1 %** (CAS No. 7697-37-2), ACS reagent grade.

**8.2.5 AA or ICP standards**, prepared in 1 % HCl solution.

**NOTE** Potential matrix interferences are seen for some metals when using HCl and ICP may be avoided by substituting 1 % HCl to 1 % HNO<sub>3</sub>.

**8.2.6 Acid mixture A**, transfer 454 g (395 mL) of concentrated hydrofluoric acid (HF 48 % w/w, ACS reagent grade) (CAS No. 7664-39-3) to a 1000 mL polyethylene bottle. Cool the bottle in ice water. While the bottle is in the ice water, add 165 mL of concentrated sulfuric acid (98 % w/w, ACS reagent grade) (CAS No. 7664-93-9). Mix and allow to cool. Add 40 mL of concentrated nitric acid (70 % w/w) (CAS No. 7697-37-2) and mix.

**WARNING** Hydrofluoric acid is corrosive and toxic. Avoid skin contact, wear protective clothing and eye/face protection, and work under a fume hood.

**8.2.7 Acid mixture B**, mix 100 mL concentrated nitric acid (70 % w/w) (CAS No. 7697-37-2) and 100 mL concentrated perchloric acid (HClO<sub>4</sub>, 72 % w/w, ACS reagent grade) (CAS No. 7601-90-3).

**WARNING** Perchloric acid is a strong and toxic acid that can cause skin burns. It can also form explosive perchlorates when reacted with other chemicals.

**8.2.8 Hydrazine sulfate solution 0.2 %** (CAS No. 10034-93-2); 0.2 g hydrazine sulfate in 100 mL deionized water.

## 8.3 Apparatus

**8.3.1 Sieve**, 150 μm (0.0059 in.-U.S. sieve No. 100).

**8.3.2 AA or ICP spectrophotometer**, any AA or ICP unit is suitable. Instrument settings recommended by the manufacturer should be followed.

**8.3.3 Analytical balance**, with accuracy of 0.001 g (1 mg).

**8.3.4 Graduated cylinder** (TD), one 25 mL.

**8.3.5 Beakers**, with covers, PTFE, or equivalent plastic, ten 100 mL.

**8.3.6 Hotplate stirrer**.

**8.3.7 Stirring bar**.

**8.3.8 Beakers**, glass, ten 400 mL.

**8.3.9 Stirring rod**, PTFE, or equivalent plastic, one end fitted with a rubber policeman.

**8.3.10 Dropper bottle**, one 25 mL.

**8.3.11 Volumetric flasks**, ten 250 mL.

**8.3.12 Polyethylene bottle**, one 1000 mL.

**8.3.13 Fume hood**.

**8.3.14 Ice bath**, for cooling acid mixture.

## 8.4 Procedure

To determine hydrofluoric, sulfuric, nitric, perchloric acid soluble metal concentrations in barite sample, the following procedure shall be applied:

NOTE Do not use glass apparatus with hydrofluoric acid solution: i.e. procedure Item a) through Item e).

- a) Use a representative sample of barite ground such that 100 % passes through the sieve.
- b) Accurately weigh a 0.50 g representative barite sample to 0.001 g (1 mg) on the analytical balance; record sample mass, expressed in g, as *m*. Transfer into a 100 mL PTFE beaker.
- c) Under a fume hood, add 15 mL of acid mixture A. Swirl the beaker to wet the sample and cover the beaker with PTFE cover.
- d) Place on the hotplate stirrer set on low heat and allow beaker to heat overnight (16 h).
- e) Remove cover from the beaker and turn heat on hotplate stirrer to ~100 °C to 150 °C (212 °F to 300 °F). Heat for 1 h or until fumes of HF are no longer released.
- f) Cool and transfer to a 400 mL beaker, using a rubber policeman and a minimum of deionized water.
- g) Place on the hotplate stirrer set on medium heat, ~100 °C to 150 °C (212 °F to 300 °F). Heat until fumes of sulfur trioxide (SO<sub>3</sub>) start to evolve, then remove beaker from the hotplate stirrer.
- h) After SO<sub>3</sub> fumes have stopped evolving, add 4 drops of acid mixture B using the dropper bottle.
- i) Replace the beaker on the hotplate stirrer and heat until strong fumes evolve and any color due to organic matter has disappeared.
- j) Remove beaker from hot plate and allow to cool for a few minutes. Then add 225 mL deionized water, 5 mL concentrated HNO<sub>3</sub>, and 1 mL of 0.2 % hydrazine sulfate solution.
- k) Replace on the hotplate stirrer and heat to boiling. If a brown precipitate of manganese dioxide (MnO<sub>2</sub>) remains after the solution has boiled for a few minutes, add an additional 1 mL of 0.2 % hydrazine sulfate.

NOTE The residue remaining should consist of BaSO<sub>4</sub> and SrSO<sub>4</sub> and should be white.

- l) Cool to room temperature. Then transfer contents of the beaker to a 250 mL volumetric flask, dilute to volume mark (250 mL) with deionized water, and mix.
- m) Allow the solids to settle. If solids do not settle, filter, or centrifuge the sample.
- n) Analyze the clear supernatant using an AA or ICP spectrophotometer. Run the standards prepared in 1 % HCl or 1 % HNO<sub>3</sub> solution. Record all values for the supernatant and standard solutions.

## 8.5 Calculation

The mass concentration of each metal shall be calculated by multiplying the results obtained on the AA or ICP spectrophotometer by the correction factor for the analyzed volume used (250/1000) and for the weight of barite sample (1000/*m*).

Metal mass concentration, soluble in HF-oxoacids,  $c_{\text{Metal-hydrofluoro,oxo ac}}$ , in barite sample, expressed in milligrams per kilogram shall be given in Equation (10).

$$c_{\text{Metal-hydrofluoro,oxo ac}} = 250 \times \left(\frac{R}{m}\right) \quad (10)$$

where

*R* is the AA or ICP reading value, expressed in milligrams per liter;

*m* is the mass of the barite sample, expressed in grams.

## 9 Alternative Methods for Iron

### 9.1 Principle

Several procedures other than those given in Section 7 and Section 8 are commonly used to determine iron concentration in barite ore bodies. The three procedures given below include two that determine acid soluble iron (one in nitric acid, the second in aqua regia) and one that determines total iron, including lattice-substituted iron (carbonate fusion).

### 9.2 Reagents and Materials

**WARNING** Concentrated acids (hydrochloric, nitric, and aqua regia) are strong, potentially harmful acids. Use proper safety precautions when handling them.

**9.2.1 Deionized or distilled water** shall be in accordance with ISO 3696 of at least Grade III.

Use deionized or distilled water for preparation of all reagents and calibration standards and as dilution water.

**9.2.2 Sodium carbonate** (CAS No. 497-19-8), ACS reagent grade.

**9.2.3 Potassium carbonate** (CAS No.584-08-7), ACS reagent grade.

**9.2.4 Sodium carbonate solution 0.2 %** (CAS No. 497-19-8); dissolve 1.0 g Na<sub>2</sub>CO<sub>3</sub> in 500 mL deionized water.

**9.2.5 Hydrochloric acid concentrated** (CAS No. 7647-01-0), 37 % w/w, ACS reagent grade.

**9.2.6 Nitric acid concentrated** (CAS No. 7697-01-0), 70 % w/w, ACS reagent grade.

**9.2.7 Aqua regia** (nitrohydrochloric acid) (CAS No. 8007-56-5); add 30 mL concentrated HNO<sub>3</sub> to 90 mL concentrated HCl.

NOTE Aqua regia shall be prepared just before to use.

**9.2.8 Nitric acid solution 1.36 mol/L** (1.36 N) (CAS No. 7697-37-2).

**9.2.9 Hydrochloric acid solution 6 mol/L**, (6N) (CAS No. 7647-01-0).

**9.2.10 Hydrochloric acid 1 % solution**, (CAS No. 7647-01-0).

**9.2.11 Iron AA or ICP standards**, prepared in 1 % HCl solution.

**9.2.12 Iron AA or ICP standards**, prepared in diluted aqua regia (add 15 mL aqua regia to 25 mL deionized water).

**9.2.13 Iron AA or ICP standards**, prepared in 1.36 mol/L (1.36 N) nitric acid.

### 9.3 Apparatus

**9.3.1 Acid digestion vessel**, stainless steel shell with a thick-walled PTFE cup and cover.

Such vessels, which are commercially available from several manufacturers, shall be leak proof and airtight when sealed, and shall be capable of withstanding operating temperatures of at least 110 °C (230 °F) and pressures of at least 1400 kPa (200 lbf/in.<sup>2</sup>). Typical capacities are in the range of 21 mL to 25 mL or higher, 45 mL.

**CAUTION** Check integrity of the cup before and after any usage. Pinhole through the lining may affect safety and may dissolve the metal body from the acid digestion bomb. Inspect the cup before any usage.

**9.3.2 Analytical balance**, with accuracy of 0.0001 g (0.1 mg).

**9.3.3 Crucibles with lids**, platinum, two 25 mL.

**9.3.4 Crucible tongs**, one 25 cm (10 in.).

**9.3.5 Filter paper**, quantitative, ash-less, medium filtration rate, grade 40 or equivalent, 110 mm circle, see 5.3.13.

**9.3.6 Filter paper**, quantitative, ash-less, medium filtration rate, grade 42 (see 6.3.14), or slow filtration rate grade 44<sup>10</sup>, 110 mm circle.

**9.3.7 Muffle furnace** regulated to 1000 °C ±20 °C (1830 °F ±35 °F).

**9.3.8 Oven**, regulated to 80 °C ±1 °C (176 °F ±2 °F).

**9.3.9 Volumetric flasks**, five 25 mL.

**9.3.10 Volumetric flasks**, five 100 mL.

**9.3.11 Beakers**, glass, five 250 mL.

**9.3.12 Filter**, borosilicate glass fiber, circle diameter 25 mm, fine particle retention (1.6 micron typical), high flow rate [fast i.e. 62 s/100 mL (Herzberg method) typical] binder free.

**9.3.13 Hot plate**.

**9.3.14 Graduated cylinder (TD)**, one 25 mL.

**9.3.15 Sieve**, 150 µm (0.0059 in.-U.S. sieve No. 100).

**9.3.16 AA spectrophotometer or ICP spectrometer**, any AA or ICP unit is suitable. Instrument settings recommended by the manufacturer should be followed.

<sup>10</sup> This grade 44 filter paper is a calendared, quantitative, ash-less filter paper made from high-quality cotton linters designed for slow to medium. The filter paper has the following typical properties which may vary by manufacturer: filtration rate: 995 s/100 mL (Herzberg method; particle retention: 3 µm (at 98 % efficiency); ash content <0.007 % by weight; basis weight: 80 g/m<sup>2</sup> (0.017 lb/ft<sup>2</sup>); thickness: 0.180 mm (0.0071 in.).

## 9.4 Nitric Acid Digestion—Iron

### 9.4.1 Procedure

To determine iron concentration in barite sample, the following nitric acid digestion procedure shall be applied.

- Use a representative sample of barite ground such that 100 % passes through the sieve.
- Accurately weight a 0.050 g (50 mg) representative barite sample to 0.0001 g ( $\pm 0.1$  mg) into acid digestion PTFE vessel (see 9.3.1). Record sample mass, expressed in g, as  $m$ .
- Add 2 mL  $\text{HNO}_3$  concentrated. Cover the PTFE digestion cup, and mount inside the steel shell. Tighten steel lid onto the bottom section.

**WARNING** Nitric acid is a strong acid. Use proper safety precautions when handling it, particularly when it is used in a digestion vessel.

- Heat for 1.5 h to 2.0 h in oven at  $80\text{ }^\circ\text{C} \pm 1\text{ }^\circ\text{C}$  ( $176\text{ }^\circ\text{F} \pm 2\text{ }^\circ\text{F}$ ).
- Cool, reheat at  $80\text{ }^\circ\text{C} \pm 1\text{ }^\circ\text{C}$  ( $176\text{ }^\circ\text{F} \pm 2\text{ }^\circ\text{F}$ ) for 1.5 h, and cool again to room temperature.
- Carefully open the bomb and dilute with deionized water by spraying a few milliliters of deionized water on the inner walls of the PTFE cell.
- Filter through grade 42 or grade 44 filter paper, into a 25 mL volumetric flask. Wash sparingly with deionized water to make a quantitative transfer. Dilute to volume mark (25 mL) with water.
- Analyze for iron using an AA or ICP spectrophotometer. Run the standards prepared in 1.36 mol/L (1.36 N)  $\text{HNO}_3$  solution. Record all values for the digested and standard solutions.

### 9.4.2 Calculation—Nitric Acid Digestion

The mass concentration of iron in barite determined by nitric acid digestion,  $c_{\text{Fe-nitric ac}}$ , expressed in milligrams per kilogram, shall be calculated by multiplying the result obtained on the AA or ICP spectrophotometer by the correction factor for the analyzed volume used (25/1000) and for weight of barite sample (1000/ $m$ ), as given in Equation (11).

$$c_{\text{Fe-nitric ac}} = 25 \times \left( \frac{R}{m} \right) \quad (11)$$

where

$R$  is the AA or ICP reading value, expressed in milligrams per liter;

$m$  is the mass of the barite sample, expressed in g.

## 9.5 Aqua Regia Digestion—Iron

### 9.5.1 Procedure

To determine iron concentration in barite sample, the following aqua regia acid digestion procedure shall be applied.

- Use a representative sample of barite ground such that 100 % passes through the sieve.
- Accurately weigh a 2.0 g representative barite sample to 0.001 g (1 mg) into acid digestion PTFE vessel (see 10.3.1). Record sample mass, expressed in g, as  $m$ .

NOTE A 45 mL acid digestion vessel should be preferred.

- c) Add 15 mL freshly prepared aqua regia. Put PTFE cover on the digestion cup and mount inside the steel shell. Seal by screwing the steel lid onto the bottom section.

**WARNING** Aqua regia is a strong acid. Use proper safety precautions when handling it, particularly when it is used in a digestion bomb.

- d) Heat for 1.5 h in oven at  $80\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$  ( $176\text{ }^{\circ}\text{F} \pm 2\text{ }^{\circ}\text{F}$ ).
- e) Cool to room temperature.
- f) Carefully open the bomb and filter the contents quantitatively through a 250 mm circle glass fiber filter into a 25 mL volumetric flask.
- g) Wash vessel, filter, and dilute to the volume mark (25 mL) with deionized water.
- h) Analyze for iron using the AA or ICP spectrophotometer. Run standards prepared in diluted aqua regia. Record all values for the digested and standard solutions.

### 9.5.2 Calculation—Aqua Regia Digestion

The mass concentration of iron in barite determined by aqua regia digestion,  $c_{\text{Fe-aq reg}}$ , expressed in milligrams per kilogram, shall be calculated by multiplying the result obtained on the AA or ICP spectrophotometer by the correction factor for analyzed volume used (25/1000) and for weight of barite sample (1000/ $m$ ), as given Equation (12).

$$c_{\text{Fe-aq reg}} = 25 \times \left( \frac{R}{m} \right) \quad (12)$$

where

- $R$  is the AA or ICP reading value, expressed in milligrams per liter;
- $m$  is the mass of the barite sample, expressed in grams.

## 9.6 Procedure—Carbonate Fusion

### 9.6.1 Procedure

To determine iron concentration in barite sample, the following carbonate fusion procedure shall be applied.

- a) Use a representative sample of barite ground such that 100 % passes through the sieve.
- b) Weigh a 0.5 g to 1.0 g representative barite sample to 0.001g (1mg). into a 25 mL platinum crucible. Record sample mass, expressed in g, as  $m$ .
- c) Mix with either 2.0 g  $\pm$ 0.1 g sodium carbonate/1.0g  $\pm$ 0.1 g potassium carbonate mix, or with 3.0 g  $\pm$ 0.1 g sodium carbonate alone. Add another 2.0 g  $\pm$ 0.1 g of carbonates to cover the mixture.
- d) Cover with a platinum lid and fuse for 1 h at 1000  $^{\circ}\text{C}$  (1830  $^{\circ}\text{F}$ ) in the muffle furnace.
- e) Remove the crucible with crucible tongs while hot and swirl gently to spread melt evenly inside the crucible.

**CAUTION** Use proper safety precautions while handling hot crucible and melts.

- f) Cool crucible and place it in a 250 mL beaker. Add sufficient deionized water to cover crucible.

- g) Place beaker on a hot plate and digest several hours on low heat until melt has completely disintegrated and separated from the platinum crucible.
- h) Completely rinse the crucible and lid with deionized water, combining the wash with the solution in the beaker.
- i) Filter through grade 40 filter paper. Wash filter paper and solids residue thoroughly with hot 0.2 % sodium carbonate solution.
- j) Dissolve the solid residue by adding hot 6mol/L (6N) hydrochloric acid to the filter paper and filtering into a 100 mL volumetric flask.
- k) Wash filter paper with deionized water and dilute to volume mark (100 mL).
- l) Analyze for iron using the AA or ICP spectrophotometer. Run standards prepared in 1 % HCl. Record all values for the carbonate fusion and standard solutions.

### 9.6.2 Calculation—Carbonate Fusion

The total mass concentration of iron in barite sample determined by carbonate fusion,  $c_{\text{Fe-carb fus}}$ , expressed in milligrams per kilogram, shall be calculated by multiplying the result obtained on the AA or ICP spectrophotometer by the correction factor for the analyzed volume used (100/1000) and for weight of barite sample (1000/ $m$ ), as given Equation (13).

$$c_{\text{Fe-carb fus}} = 100 \times \left( \frac{R}{m} \right) \quad (13)$$

where

- $R$  is the AA or ICP reading value, expressed in milligrams per liter;  
 $m$  is the mass of the barite sample, expressed in grams.

## 10 Water-soluble Materials in Barite

### 10.1 Principle

The water-soluble material in most barite is less than 0.1 % (1000 mg/kg) and consists mostly of the chlorides, sulfates, and carbonates of sodium and potassium, and of the chlorides and sulfates of calcium and magnesium. As far as the use of barite in drilling fluid is concerned, only the soluble alkaline earth metals (primarily calcium and magnesium) are of essential importance. Specification for calcium and magnesium reported as calcium is 250 mg/kg maximum. Soluble zinc, manganese, copper, lead, and chromium are often determined for environmental purposes.

### 10.2 Apparatus and Materials

**10.2.1 Sieve**, 150  $\mu\text{m}$  (0.0059 in.-U.S. sieve No. 100).

**10.2.2 AA spectrophotometer** or **ICP spectrometer**, any AA or ICP unit is suitable. Instrument settings recommended by the manufacturer should be followed.

**10.2.3 Analytical balance**, with accuracy of 0.001 g.

**10.2.4 Mechanical shaker**, or magnetic stirrer with stirring bar, or field mixer with powerstat.

**10.2.5 Graduated cylinder** (TD), one 100 mL.

**10.2.6 Conical flask** (Erlenmeyer), one 250 mL.

**10.2.7 API low-pressure filter** cell shall be as described in API 13B-1.

**10.2.8 Volumetric flask**, one 200 mL.

**10.2.9 Cork or rubber stopper**, to fit conical flask.

**10.2.10 Deionized or distilled water** shall be in accordance with ISO 3696 of at least Grade III.

Use deionized or distilled water for preparation of all reagents and calibration standards and as dilution water.

### 10.3 Procedure—Water-soluble Materials in Barite

#### 10.3.1 General

Water-soluble materials in a barite sample shall be determined after preparation of a water-leachate filtrate, then, following analysis shall be performed on the filtrate:

- a) Analyze for calcium, magnesium, zinc, manganese, copper, lead, and chromium using an AA or ICP spectrophotometer (see 10.4).
- b) Analyze for sodium and potassium using a flame photometer, an AA spectrometer in the flame emission mode or ICP spectrometer (see 10.4).
- c) Analyze the for chlorides using silver nitrate titration or IC method (Section 11).
- d) Analyze for sulfates using turbidity method or IC method (Section 12).
- e) Analyze for carbonates, bicarbonates, and hydroxyl using standard acid titration (Section 13).
- f) Analyze for phosphates using a colorimetric method (Section 14).

#### 10.3.2 Barite Water-leachate Preparation

To determine water-soluble materials in barite sample, the following procedure shall be applied to prepare a barite water-leachate filtrate to be analyzed.

- a) Use a representative sample of barite ground such that 100 % passes through the sieve.
- b) Accurately weigh a 100.0 g barite sample to 0.001 g (1 mg). Record sample mass, expressed in g as  $m$ .
- c) Transfer to a 250 mL Erlenmeyer flask. Add 100 mL of deionized water.
- d) Stopper and shake on a mechanical shaker for 30 min.
- e) Filter the suspension using an API low-pressure filter cell into a graduated cylinder.
- f) Transfer barite water-leachate filtrate to a 250 mL volumetric flask, wash sides of graduated cylinder, transferring washings to flask and dilute to volume mark (250 mL) with deionized water.

NOTE It shall result 250 mL filtrate volume prepared with  $m$  grams of barite, equivalent to  $4m$  grams of barite per liter of water-leachate filtrate.

## 10.4 Water-soluble Metals in Barite

Water-soluble calcium, magnesium, zinc, manganese, copper, lead, and chromium concentrations shall be determined by an AA or ICP chromatography analysis on the barite water-leachate as prepared in 10.3.2.

Water-soluble sodium and potassium concentrations shall be determined by an AA spectrometer in the flame emission mode or an ICP spectrometer analysis on the barite water-leachate as prepared in 10.3.2.

Necessary dilutions, pH adjustments, and matrix matching between samples and standards shall be made.

NOTE For very low metal concentrations, it may be necessary to use a graphite furnace or ICP spectrometer.

## 10.5 Calculation—Water-soluble Materials in Barite

Metal mass concentrations in barite sample from water-soluble metals,  $c_{\text{Metal-aq}}$ , expressed in milligrams per kilogram, shall be calculated by multiplying the results obtained on the AA or ICP spectrophotometer for metal-ion by the correction factor for weight of barite sample to prepare water-leachate filtrate sample ( $4m$  g/L), as given in Equation (14).

$$c_{\text{Metal-aq}} = 1000 \times \frac{R}{4m} = 250 \times \left(\frac{R}{m}\right) \quad (14)$$

where

$R$  is the AA or ICP reading value, expressed in milligrams per liter;

$m$  is the mass of the barite sample (10.3.2), expressed in grams.

NOTE If a dilution was made in analyzing the prepared water-leachate filtrate sample, multiply the results on the AA spectrophotometer by the correction factor for the dilution made.

Mass concentrations for calcium, magnesium, zinc, manganese, copper, lead, and chromium shall be determined using an AA or ICP spectrophotometer.

Mass concentrations for sodium and potassium shall be determined using a flame photometer, an AA spectrometer in the flame emission mode or an ICP spectrometer.

## 11 Water-soluble Chlorides

### 11.1 Principle

The concentration of water-soluble chlorides shall be measured by silver nitrate titration or ion chromatography (IC) on a sample of barite water-leachate filtrate prepared according to 10.3.2.

### 11.2 Reagents and Materials

**11.2.1 Silver nitrate solution** (CAS No. 7761-88-8), 0.0282 mol/L (0.0282N), ACS reagent grade. Dissolve 4.7910 g silver nitrate in deionized water and dilute to a volume of one liter. Shall be stored in an amber or opaque bottle. One milliliter of silver nitrate solution is equivalent to 0.001 g (1 mg) chloride-ion.

**11.2.2 Potassium chromate indicator** (CAS NO. 7664-00-6). Dissolve 5 g  $\text{K}_2\text{CrO}_4$  in 100 mL deionized water, stored in dropper bottle.

**11.2.3 Sulfuric acid** (CAS No. 7664-93-9), 0.01 mol/L (N/50), ACS reagent grade.

**WARNING** Concentrated sulfuric acid is a strong, potentially harmful acid. Use proper safety precautions when handling it.

**11.2.4 Phenolphthalein indicator** (CAS No. 77-09-8); 1.0 g phenolphthalein in 100 mL of 50:50 ethyl alcohol/deionized water mix, stored in dropper bottle.

**11.2.5 Deionized or distilled water** shall be in accordance with ISO 3696 of at least Grade III.

Use deionized or distilled water for preparation of all reagents and calibration standards and as dilution water.

**11.2.6 Chloride ion chromatograph standards**, 1 mg/L, 5 mg/L, and 10 mg/L chloride in deionized water.

### 11.3 Apparatus

**11.3.1 Serological pipettes** (TD), graduated, one 1 mL and one 10 mL.

**11.3.2 Titration vessel**, 100 mL to 150 mL beaker or conical flask (Erlenmeyer), preferably white.

**11.3.3 Stirring rod or Magnetic stirrer with stirring bar** (preferred).

**11.3.4 Burette**, one 10 mL.

**11.3.5 Ion chromatograph**, any ion chromatograph unit with settings recommended by manufacturer, is suitable.

### 11.4 Procedure—Water-soluble Chlorides by Titration

Concentration of water-soluble chlorides shall be determined by the following titration procedure.

- a) Pipette one or more milliliters of barite water-leachate filtrate from 10.3.2, recorded as volume  $V$ , into the titration vessel.

NOTE Barite water-leachate filtrate volume: 250 mL.

- b) Add 2 drops or 3 drops of phenolphthalein solution. If the indicator turns pink, add 0.01 mol/L sulfuric acid drop by drop from a pipette, while stirring, until the color is discharged.
- c) Add 25 mL of deionized water and 5 drops to 10 drops of potassium chromate indicator.
- d) While stirring continuously, titrate the solution slowly (dropwise) with standard silver nitrate solution until the color changes from yellow to orange-red and persists for 30 s. Record the volume of silver nitrate solution,  $V_{\text{AgNO}_3}$ , required to reach the end point.
- e) If the volume of silver nitrate used in titration shall be between 1 mL and 10 mL. If it is not the case, adjust the volume of barite water-leachate filtrate ( $V$ ), Item a) and repeat the procedure through Item d).

### 11.5 Procedure—Water-soluble Chlorides by Ion Chromatography

Concentrations of water-soluble chlorides shall be determined by the following IC procedure.

- a) Use a suitable amount of barite water-leachate filtrate from 10.3.2, for the analysis.

NOTE Barite water-leachate filtrate volume: 250 mL.

- b) Analyze the filtrate for chlorides by IC using manufacturer accepted instrument settings and procedures.

NOTE Water-soluble sulfates (see 12.6) may also be determined at the same time.

- c) Analyze standards prepared in deionized water.
- d) Record all values and correct for any dilutions made if required.

## 11.6 Calculation—Water-soluble Chlorides

### 11.6.1 Water-soluble Chlorides by Titration

Mass concentration of water-soluble chlorides in barite sample,  $c_{\text{Cl-aq}}$ , determined by titration expressed in milligrams per kilogram, shall be given in Equation (15). Equation coefficient takes in account the weight of barite sample ( $m$ ) to prepare the water-leachate filtrate sample (250 mL) and the volume of filtrate sample ( $V$ ).

$$c_{\text{Cl-aq}} = 1000 \times \frac{250}{m} \times \frac{V_{\text{AgNO}_3}}{V} = 2.5 \times 10^5 \times \left( \frac{V_{\text{AgNO}_3}}{mV} \right) \quad (15)$$

where

- $V_{\text{AgNO}_3}$  is the volume of silver nitrate used, expressed in milliliters (equivalent to milligrams of chlorides);
- $V$  is the volume of barite water-leachate filtrate sample used for titration (see 10.3.2), expressed in milliliters;
- $m$  is the mass of the barite sample (see 10.3.2), expressed in grams.

### 11.6.2 Water-soluble Chlorides by Ion Chromatography

Mass concentration of water-soluble chlorides in barite sample,  $c_{\text{Cl-aq}}$ , determined by IC, expressed in milligrams per kilogram shall be given in Equation (16). Equation coefficient takes in account the weight of barite sample to prepare the water-leachate filtrate sample (4m g/L).

$$c_{\text{Cl-aq}} = 1000 \times \frac{R_{\text{IC}}}{4m} = 250 \times \left( \frac{R_{\text{IC}}}{m} \right) \quad (16)$$

where

- $R_{\text{IC}}$  is the measured value from ion chromatograph, expressed in milligrams per liter;
- $m$  is the mass of the barite sample (10.3.2), expressed in grams.

## 12 Water-soluble Sulfates

### 12.1 Principle

The water-soluble sulfates are analyzed by turbidimetry using the reaction of soluble sulfates with barium chloride or by IC on a sample of barite water-leachate filtrate prepared according to 10.3.2.

### 12.2 Reagents and Materials

**12.2.1 Hydrochloric acid solution** 6 mol/L (6N), (CAS No. 7647-01-0); ACS reagent grade.

**WARNING** Concentrated hydrochloric acid is a strong, potentially harmful acid. Use proper safety precautions when handling it.

**12.2.2 Sodium sulfate**, anhydrous (CAS No. 7757-82-6), ACS reagent grade.

**12.2.3 Barium chloride** (dihydrate) (CAS No. 10361-37-2), ACS reagent grade crystals.

**WARNING** Barium chloride is extremely toxic. Avoid any contact with it that could lead to ingestion.

**12.2.4 Deionized or distilled water** shall be in accordance with ISO 3696 of at least Grade III.

Use deionized or distilled water for preparation of all reagents and calibration standards and as dilution water.

**12.2.5 Sulfate ion chromatograph standards**, 1 mg/L, 5 mg/L, and 10 mg/L sulfates in deionized water.

### 12.3 Apparatus

**12.3.1 Spectrophotometer**, filter photometer, or turbidimeter, with proper cells for the meter of choice. Use spectrophotometer at a wavelength of 420 nm.

**12.3.2 Analytical balance**, with an accuracy of 0.0001 g (0.1 mg).

**12.3.3 Volumetric flasks**, one 1000 mL, four 100 mL.

**12.3.4 Beakers**, seven 50 mL.

**12.3.5 Graduated cylinder (TD)**, one 10 mL.

**12.3.6 Timer**, accurate at  $\pm 5$  s per hour.

**12.3.7 Pipettes**, one 10 mL, one 5 mL, one 20 mL.

**12.3.8 Cuvettes**, or appropriate container for transmission or turbidimetric analysis.

**12.3.9 Graph paper**, linear.

**12.3.10 Ceramic sampling spoon**, capacity 1 mL.

**12.3.11 Ion chromatograph**, any ion chromatograph unit with settings recommended by manufacturer, is suitable.

### 12.4 Procedure—Preparation of Calibration Chart for Turbidity Method

Calibration curve for turbidity method shall be prepared as per the following procedure.

- a) Weigh out 0.1480 g  $\pm 0.0001$  g of sodium sulfate. Transfer quantitatively to 1000 mL volumetric flask. Add  $\sim 100$  mL deionized water, mix to dissolve, and dilute to volume mark. Mix well. This is the stock solution containing 100 mg/L  $\text{SO}_4^{-2}$ .
- b) Prepare 20 mg/L, 40 mg/L, 60 mg/L, and 80 mg/L  $\text{SO}_4^{-2}$  standard solution by pipetting 20 mL, 40 mL, 60 mL, and 80 mL of stock solution into separate 100 mL volumetric flasks and making up to volume with deionized water. Mix well.
- c) Pipette 15 mL of each standard (i.e.  $V$  the volume of test sample, see 12.5) and the stock solution into separate dry, clean 50 mL beakers. Add 1 mL 6 mol/L HCl to each solution. Swirl gently to mix.
- d) Add  $\sim 0.3$  g to 0.4 g [half a spoonful (see 12.3.10)] of barium chloride crystals to each beaker. Swirl gently to mix.
- e) Let samples stand 4 min  $\pm 15$  s.
- f) Prepare a reagent blank by pipetting 15 mL deionized water into another clean, dry 50 mL beaker, add 1 mL 6 mol/L HCl, and swirl to mix. Add  $\sim 0.3$  g to 0.4 g [half a spoonful (see 12.3.10)] of barium chloride crystals. Swirl to mix.
- g) Transfer the blank solution to a sample cell, insert cell in instrument, and record the absorbance reading.
- h) Repeat Item g) with the other standard solutions prepared as per 12.4 Item b) through Item e).

- i) Plot the absorbance readings versus the  $\text{SO}_4^{-2}$  standard expressed in milligrams per liter (mg/L), using linear graph paper.

### 12.5 Procedure—Analysis for Water-soluble Sulfates by Turbidity Method

To determine concentration of water-soluble sulfates in barite sample, by turbidity method the following procedure shall be applied.

- a) Pipette 15 mL of barite water-leachate filtrate from 10.3.2 ( $V$  test sample volume) into a clean 50 mL beaker. Add 1 mL 6 mol/L HCl. Swirl gently to mix.

NOTE Barite water-leachate filtrate total prepared volume: 250 L.

- b) Add ~0.3 g to 0.4g [half a spoonful (see 12.3.10)] of barium chloride crystals. Swirl gently to mix.
- c) Let sample stand 4 min  $\pm$ 15s.
- d) Transfer the solution to a sample cell, insert cell in instrument, and record the absorbance reading.
- e) Use the calibration chart (see 12.4) to convert the absorbance reading to  $\text{SO}_4^{-2}$  concentration expressed in milligrams per liter. If sample concentration is higher than highest standard, make the proper dilution and repeat the analysis.

### 12.6 Procedure—Analysis for Water-soluble Sulfate by Ion Chromatography

To determine mass concentration of water-soluble sulfates in barite sample by IC the following procedure shall be applied.

- a) Use a suitable amount of barite water-leachate filtrate from 10.3.2 for the analysis.

NOTE Barite water-leachate filtrate total prepared volume: 250 mL

- b) Analyze the barite water-leachate filtrate for sulfates by IC using manufacturer accepted instrument settings and procedures. Analyze standards prepared in deionized water.
- c) Record all values and correct for any dilutions made if required.

### 12.7 Calculation—Water-soluble Sulfates

#### 12.7.1 Water-soluble Sulfates by Turbidity Method

Mass concentration of water-soluble sulfates in barite sample,  $c_{\text{SO}_4\text{-aq}}$ , determined by turbidity method, expressed in milligrams per kilogram shall be given in Equation (17). Equation coefficient takes in account the weight of barite sample to prepare the water-leachate filtrate ( $4m$  g/L).

$$c_{\text{SO}_4\text{-aq}} = 1000 \times \frac{R_M}{4m} = 250 \times \left( \frac{R_M}{m} \right) \quad (17)$$

where

- $m$  is the mass of barite sample (10.3.2), expressed in grams;
- $R_M$  is the turbidimeter reading, expressed in milligrams per liter.

### 12.7.2 Water-Soluble Sulfates by Ion Chromatography

Mass concentration of water-soluble sulfates in barite sample,  $c_{\text{SO}_4\text{-aq}}$ , determined by IC, expressed in milligrams per kilogram shall be given in Equation (18). Equation is corrected by the factor for dilution and the weight of barite sample to prepare the water-leachate filtrate sample ( $4m$  g/L).

$$c_{\text{SO}_4\text{-aq}} = 1000 \times \frac{R_{\text{IC}}}{4m} \times = 250 \times \left( \frac{R_{\text{IC}}}{m} \right) \quad (18)$$

where

$R_{\text{IC}}$  is the measured value from ion chromatograph, expressed in milligrams per liter;  
 $m$  is the mass of barite sample (10.3.2), expressed in grams.

## 13 Water-soluble Carbonates, Bicarbonates, and Hydroxyl Ions

### 13.1 Principle

Carbonates, bicarbonates, and hydroxyl ion concentrations are determined from the amount of standard acid required to titrate a given amount of barite water-leachate filtrate prepared according to 10.3.2 to the phenolphthalein and methyl orange end points.

### 13.2 Reagents and Materials

**13.2.1 Sulfuric acid solution**, 0.01 mol/L (N/50)  $\text{H}_2\text{SO}_4$  (CAS No. 7664-93-9), ACS reagent grade.

**WARNING** Sulfuric acid is a strong, potentially harmful acid. Use proper safety precautions when handling it.

**13.2.2 Phenolphthalein indicator** (CAS No. 77-09-8), 1.0 g phenolphthalein to 100 mL of 50:50 ethyl alcohol/deionized water solution, stored in dropper bottle.

**13.2.3 Methyl orange indicator** (CAS No.547-58-0), 0.1 g methyl orange to 100 mL deionized water, stored in dropper bottle.

### 13.3 Apparatus

**13.3.1 pH meter** (optional, but more accurate procedure).

**13.3.2 Titration vessel**, 100 mL to 150 mL, preferably white.

**13.3.3 Serological pipette** (TD), graduated, one 10 mL.

**13.3.4 Volumetric pipettes**, one 10 mL and one 25 mL.

**13.3.5 Stirring rod** or **magnetic stirrer** with stirring bar.

### 13.4 Procedure

To determine concentrations of water-soluble carbonates, bicarbonates, and hydroxyl ions in barite water-leachate filtrate by standard acid titration, the following procedure shall be applied.

- a) Pipette 10 mL sample of barite water-leachate filtrate from 10.3.2 into an appropriately sized beaker. (Use a 25 mL sample, if necessary). Record volume as  $V$ .

NOTE Barite water-leachate filtrate total prepared volume: 250 mL.

- b) Add 2 drops of phenolphthalein indicator and titrate to the colorless end point with 0.01 mol/L (N/50) H<sub>2</sub>SO<sub>4</sub>. This is at pH 8.3 if using a pH meter. Record the number of milliliters of acid required, as  $P_f$ .

NOTE If no color change is observed after addition of phenolphthalein, sample is devoid of water-soluble carbonates.

- c) Add 2 drops of methyl orange indicator and, without refilling the pipette, continue the titration to the methyl orange end point, noted by the solution changing from green to purple. This is at pH 4.3 if using a pH meter. Record the number of milliliters of H<sub>2</sub>SO<sub>4</sub> acid required, as  $M_f$  (including that amount required for the  $P_f$  end points).

### 13.5 Calculation

#### 13.5.1 Alkalinity Values and Water-soluble Carbonates, Bicarbonates, and Hydroxyl

According to the relationship between phenolphthalein alkalinity ( $P_f$ ) and methyl orange alkalinity ( $M_f$ ), it shall be possible to determine the nature of water-soluble ions in the tested barite water-leachate filtrate sample.

- If  $P_f = 0$  the alkalinity is due to bicarbonate ion (HCO<sub>3</sub><sup>-</sup>) alone;
- If  $P_f = M_f$  the alkalinity is due to hydroxyl ion (OH<sup>-</sup>) alone;
- If  $2 P_f = M_f$  the alkalinity is due to carbonate ion (CO<sub>3</sub><sup>2-</sup>) alone;
- If  $2 P_f > M_f$  the alkalinity is due to a mixture of carbonate (CO<sub>3</sub><sup>2-</sup>) and hydroxyl ions (OH<sup>-</sup>);
- If  $2 P_f < M_f$  the alkalinity is due to a mixture of carbonate (CO<sub>3</sub><sup>2-</sup>) and bicarbonate ions (HCO<sub>3</sub><sup>-</sup>).

#### 13.5.2 Mass Concentration Calculations

Mass concentrations of carbonates, bicarbonates, and hydroxyl ions in barite sample expressed in milligrams per kilogram shall be given in Equation (19) through Equation (25). Equations take in account the weight of barite sample to prepare the water-leachate filtrate sample ( $4m$  g/L) and the volume of filtrate sample ( $V$ ).

- a) Mixture of carbonate and bicarbonate ions (case  $2 P_f < M_f$ )

- Carbonate mass concentration,  $c_{\text{CO}_3}$ , expressed in milligrams per kilogram as given in Equation (19).

$$c_{\text{CO}_3} = \frac{1000}{4m} \times \frac{1}{V} \times (1200 \times P_f) = 3 \times 10^5 \times \left( \frac{P_f}{mV} \right) \quad (19)$$

- Bicarbonate mass concentration,  $c_{\text{HCO}_3}$ , expressed in milligrams per kilogram as given in Equation (20).

$$c_{\text{HCO}_3} = \frac{1000}{4m} \times \frac{1}{V} \times [1220 \times (M_f - 2P_f)] = 3.05 \times 10^5 \times \frac{(M_f - 2P_f)}{mV} \quad (20)$$

- b) Carbonate ion alone (case  $2 P_f = M_f$ ).

Carbonate mass concentration,  $c_{\text{CO}_3}$ , expressed in milligrams per kilogram is given in Equation (21).

$$c_{\text{CO}_3} = \frac{1000}{4m} \times \frac{1}{V} \times (1200 \times P_f) = 3 \times 10^5 \times \left( \frac{P_f}{mV} \right) \quad (21)$$

- c) Mixture of carbonate and hydroxyl ions (case  $2 P_f > M_f$ ).

1) Carbonate mass concentration,  $c_{\text{CO}_3}$ , expressed in milligrams per kilogram as given in Equation (22).

$$c_{\text{CO}_3} = \frac{1000}{4m} \times \frac{1}{V} \times [1200 \times (M_f - P_f)] = 3 \times 10^5 \times \left( \frac{M_f - P_f}{mV} \right) \quad (22)$$

2) Hydroxyl mass concentration,  $c_{\text{OH}}$ , expressed in milligrams per kilogram as given in Equation (23).

$$c_{\text{OH}} = \frac{1000}{4m} \times \frac{1}{V} \times [340 \times (2P_f - M_f)] = 8.5 \times 10^4 \times \left( \frac{2P_f - M_f}{mV} \right) \quad (23)$$

d) Bicarbonate ion alone (case  $P_f = 0$ ).

Bicarbonate mass concentration,  $c_{\text{HCO}_3}$ , expressed in milligrams per kilogram as given in Equation (24).

$$c_{\text{HCO}_3} = \frac{1000}{4m} \times \frac{1}{V} \times (1220 \times M_f) = 3.05 \times 10^5 \times \left( \frac{M_f}{mV} \right) \quad (24)$$

e) Hydroxyl ion alone (case  $P_f = M_f$ ).

Hydroxyl mass concentration,  $c_{\text{OH}}$ , expressed in milligrams per kilogram as given in Equation (25).

$$c_{\text{OH}} = \frac{1000}{4m} \times \frac{1}{V} \times (340 \times M_f) = 8.5 \times 10^4 \times \left( \frac{M_f}{mV} \right) \quad (25)$$

where

$V$	is the volume of barite water-leachate filtrate sample, expressed in milliliters;
$m$	is the mass of the barite sample (see 10.3), expressed in grams;
$M_f$	is the volume of 0.01 mol/L (0.02N) $\text{H}_2\text{SO}_4$ used in titration to reach methyl orange end point, expressed in milliliters;
$P_f$	is the volume of 0.01 mol/L (0.02N) $\text{H}_2\text{SO}_4$ used in titration to reach phenolphthalein end point, expressed in milliliters.

## 14 Water-soluble Phosphates

### 14.1 Principle

Water-soluble phosphates, both ortho and condensed, are determined by a colorimetric analysis and use of premix phosphate reagents for ascorbic acid method (such as PhosVer III<sup>11</sup> or equivalent). A sample of the barite water-leachate filtrate from Section 10 is heated in the presence of excess acid to convert all phosphates to orthophosphate. Color is developed by the addition of phosphate reagent, which contains ammonium molybdate and ascorbic acid. An intense blue color is formed if phosphate is present, and the intensity of the color is measured with a spectrophotometer at a wavelength of 700 nm. IC may be used as an alternative for phosphate determinations.

### 14.2 Reagents and Materials

**14.2.1 Sulfuric acid solution, 2.63 mol/L (5.25 N) (CAS No.7664-93-9); ACS reagent grade.**

<sup>11</sup> PhosVer III® is an example of a suitable product available commercially. This information is given for the convenience of the users of this part of API 13K and does not constitute an endorsement by API of this product.

**WARNING** Concentrated sulfuric acid is a strong, potentially harmful acid. Use proper safety precautions when handling it.

**14.2.2 Sodium hydroxide solution**, 5 mol/L (5N) (CAS No.1310-73-2); 200 g NaOH (ACS reagent grade) to 1000 mL solution.

**WARNING** Concentrated sodium hydroxide is a strong, potentially harmful alkali. Use proper safety precautions when handling it.

**14.2.3 Sodium phosphate** (CAS #10361-03-2), ( $\text{NaPO}_4 \cdot 12\text{H}_2\text{O}$ ), ACS reagent grade.

**14.2.4 Standard phosphate stock solution** (CAS No. 10361-03-2), 1000 mg/L  $\text{PO}_4^{-3}$ , 1.7260 g  $\pm 0.0001$  g sodium phosphate in 1 L solution.

**14.2.5 Phosphate reagent powder**, ascorbic acid method, (PhosVer III<sup>12</sup> or equivalent), pillows.

**14.2.6 Deionized or distilled water** shall be in accordance with ISO 3696 of at least Grade III.

Use deionized or distilled water for preparation of all reagents and calibration standards and as dilution water.

### 14.3 Apparatus

**14.3.1 Spectrophotometer or filter photometer**, capable of measuring absorbance at a wavelength of 700 nm.

**14.3.2 Analytical balance**, with an accuracy of 0.0001 g (0.1 mg).

**14.3.3 Conical flask** (Erlenmeyer), several 125 mL.

**14.3.4 Graduated mixing cylinders**, with stoppers, several 25 mL.

**14.3.5 Volumetric pipettes**, several of various sizes.

**14.3.6 Volumetric flask**, several 100 mL.

**14.3.7 Hot plate**.

**14.3.8 Graph paper**, linear.

### 14.4 Procedure—Preparation of Calibration Curve

Calibration curve for water-soluble phosphates colorimetry determination shall be prepared as per the following procedure.

- Prepare standard solutions containing 0.25 mg/L, 0.50 mg/L, 1.00 mg/L, and 2.00 mg/L  $\text{PO}_4^{-3}$  by serial dilution of the stock phosphate standard solution.
- Transfer 25 mL of each standard solution to a 125 mL conical flask. Prepare a reagent blank using 25 mL of deionized water.
- Add 2.0 mL of 2.63 mol/L sulfuric acid and boil gently on a hot plate for 30 min, maintaining sample volume at 15 mL to 20 mL by additions of deionized water.
- After 30 min, remove from the hot plate, cool to room temperature, add 2.0 mL of 5 mol/L sodium hydroxide solution, and transfer to the 25 mL graduated mixing cylinders.

<sup>12</sup> PhosVer III powder pillows® are an example of a suitable product available commercially. This information is given for the convenience of users of this part of API 13K and does not constitute an endorsement by API of these products.

- e) Add the contents of one phosphate reagent pillow, dilute to the 25 mL mark with deionized water. Stopper and mix.
- f) Wait at least 2 min but no more than 10 min, then measure the absorbance at the wavelength of 700 nm, using a sample cell or tube with a path length of 25 mm (1 in.). Zero the instrument using the reagent blank.
- g) Prepare a calibration curve by plotting phosphate ion concentration versus absorbance on linear graph paper.

#### 14.5 Procedure—Analysis of Sample

To analyze barite water-leachate filtrate for water-soluble phosphates, the following procedure shall be applied.

- a) Transfer 5 mL of the barite water-leachate filtrate sample prepared according to 10.3.2 to a 125 mL conical flask, record sample volume as  $V$ . Add sufficient deionized water to bring total volume to 25 mL.

NOTE Barite water-leachate filtrate total prepared volume: 250 mL.

- b) Proceed with procedure 14.4 Item c) through Item f).
- c) Determine the phosphate content, in milligrams per liter, in the final 25 mL solution by reference to the previously prepared calibration curve.
- d) If the phosphate ion content is below the range of the calibration curve, take a larger portion of the barite water-leachate prepared according to 10.3.2. If the phosphate ion content is above the range of the calibration curve, prepare a volumetric dilution and take an appropriate aliquot. In any case, record the actual volume,  $V$ , of the original water-leachate filtrate that was present in the solution in which the color was developed.

#### 14.6 Calculation

Mass concentration of water-soluble phosphates in barite sample,  $c_{\text{PO}_4}$ , expressed in milligrams per kilogram shall be given Equation (26). Equation coefficient takes in account the final measured volume (25 mL), the weight of barite sample to prepare the water-leachate filtrate ( $4m$  g/L), and the volume of filtrate sample ( $V$ ).

$$c_{\text{PO}_4} = 1000 \times \frac{1000}{4mV} \times \frac{25 \times R_{\text{PO}_4}}{1000} = 6250 \times \left( \frac{R_{\text{PO}_4}}{mV} \right) \quad (26)$$

where

- $R_{\text{PO}_4}$  is the phosphate ion concentration reading from the calibration curve, expressed in milligrams per liter;
- $V$  is the volume of barite water-leachate filtrate sample, expressed in milliliters;
- $m$  is the mass of the barite sample (see 10.3), expressed in grams.

### 15 Loss on Ignition (LOI)

#### 15.1 Principle

The *LOI* of barite ores is the weight loss after heating to 1000 °C (1830 °F). The *LOI* can be due to several things, including the following.

- a) Moisture—rarely over 0.1 % to 0.2 %, and usually not separately determined.
- b) Combined water—from clays, hydrated iron oxides, gypsum, and other accessory minerals.

- c) Organic and carbonaceous matter.
- d) Thermal decomposition of carbonate minerals. This can be offset by the metal oxides formed combining with sulfur oxides to form metal sulfides.
- e) Loss of sulfur from decomposition of pyrite. This can be offset by the iron taking up oxygen.

## 15.2 Reagents, Materials, and Apparatus

**15.2.1 Desiccant**, silica gel (CAS No.7631-86-9), indicating.

**15.2.2 Sieve**, 150  $\mu\text{m}$  (0.0059 in.-U.S. sieve No. 100).

**15.2.3 Analytical balance**, with an accuracy of 0.0001 g (0.1 mg).

**15.2.4 Crucibles and lids**, platinum, two 25 mL.

**15.2.5 Muffle furnace**, regulated to 1000  $^{\circ}\text{C} \pm 20^{\circ}\text{C}$  (1830  $^{\circ}\text{F} \pm 35^{\circ}\text{C}$ ).

**15.2.6 Desiccator**, glass.

## 15.3 Procedure

The following procedure shall be applied to determine *LOI* of barite.

- a) Use a representative sample of barite ground such that 100 % passes through the sieve.
- b) Accurately weigh an ignited platinum crucible to 0.0001 g (0.1 mg). Record weight, expressed in g, as  $m_3$ .
- c) Accurately weight a 1.0 g to 1.5 g barite sample to 0.0001 g (0.1 mg) into an ignited platinum crucible. Record sample mass plus crucible, expressed in g, as  $m_4$ .
- d) Cover with lid and place crucible into a cold muffle furnace. Heat to 1000  $^{\circ}\text{C}$  (1830  $^{\circ}\text{F}$ ) and hold at 1000  $^{\circ}\text{C}$  (1830  $^{\circ}\text{F}$ ) for 30 min.
- e) Cool in desiccator. Remove lid and reweigh accurately on the analytical balance. Record this mass of ignited sample plus crucible, expressed in g, as  $m_5$ .

## 15.4 Calculation

Barite sample loss on ignition, *LOI*, expressed as a percentage shall be given in Equation (27).

$$LOI = 100 \times \frac{(m_4 - m_5)}{(m_4 - m_3)} \quad (27)$$

where

- $m_3$  is the mass of the crucible, expressed in grams;
- $m_4$  is the mass of barite sample and crucible, expressed in grams;
- $m_5$  is the mass of ignited sample and crucible, expressed in grams.

## 16 Siderite Content

### 16.1 Principle

Siderite ( $\text{FeCO}_3$ ) occurs in barite as a natural impurity. Siderite can be dissolved from the barite matrix by refluxing the barite with an alkaline solution of tetrasodium ethylene diamine tetraacetic acid (EDTA) and then analyzing by either AA, ICP spectrometry, or colorimetry.

### 16.2 Reagents and Materials

**16.2.1 Distilled or deionized water** shall be in accordance with ISO 3696 of at least Grade III.

Use deionized or distilled water for preparation of all reagents and calibration standards and as dilution water.

**16.2.2 Sodium hydroxide solution** 8 mol/L (8N), (CAS No. 1310-73-2) 320 g NaOH, ACS reagent grade, in 1 L deionized water.

**WARNING** Concentrated sodium hydroxide is a strong, potentially harmful alkali. Use proper safety precautions when handling it.

**16.2.3 EDTA solution**, (CAS No. 64-02-8), ACS reagent grade; 40 g  $\text{Na}_4\text{EDTA}$  in 100 mL deionized water.

If tetrasodium salt is not available, EDTA solution may be prepared from disodium salt. Into a 500 mL beaker, add 325 mL deionized water, 196.0 g  $\text{Na}_2\text{H}_2\text{EDTA}\cdot 2\text{H}_2\text{O}$  (CAS No. 6388-92-6) and 37.5 g NaOH. Dissolve and adjust pH to 11.0 with NaOH solution 8 mol/L (8N). Dilute to 500 mL with deionized water.

**16.2.4 Hydrochloric acid solution** 1 mol/L (1N) (CAS No. 7647-01-0), ACS reagent grade.

**16.2.5 Iron reagent powder**, colorimetric phenantroline method (FerroVer<sup>13</sup> or equivalent), pillows, 0 mg/L to 3 mg/L range.

**16.2.6 AA or ICP iron standards.**

### 16.3 Apparatus

**16.3.1 Balance**, with an accuracy of 0.1 g.

**16.3.2 Flask**, round bottom, 250 mL.

**16.3.3 Condenser**, water-cooled.

**16.3.4 Heating mantle**, to fit 250 mL round-bottom flask.

**16.3.5 Variable power regulator.**

**16.3.6 Funnel**, 77 mm (3 in.).

**16.3.7 Filter paper**, qualitative, standard cellulose, medium retention and filtration rate, grade 1<sup>14</sup> or equivalent, 110 mm circle.

**16.3.8 AA spectrophotometer**, or **ICP spectrometer**, or equivalent.

<sup>13</sup> FerroVer® powder pillows are an example of a suitable product available commercially. This information is given for the convenience of users of this part of API 13K and does not constitute an endorsement by API of these products.

<sup>14</sup> This standard cellulose grade 1 filter paper is designed for medium retention and filtration rate. The filter paper has the following typical properties that may vary by manufacturer: filtration rate 150 s/100 mL (Herzberg method, particle retention in liquid 11  $\mu\text{m}$  (at 98 % efficiency); weight 87 g/m<sup>2</sup> (0.019 lb/ft<sup>2</sup>); thickness 0.180 mm (0.0071 in.).

**16.3.9 Spectrocolorimeter**, scale and filter for iron analysis.

**16.3.10 Volumetric flask**, one 1 L.

#### 16.4 Procedure—EDTA Extraction

Extraction shall be performed by the following procedure.

- a) Weight a 20.0 g representative barite sample to 0.1 g. Record the sample mass, expressed in g, as  $m$ .
- b) Add the weighed sample to the 250 mL extraction flask. To the flask add 100 mL EDTA extraction solution (see 16.2.4).
- c) Adjust pH to 11.0 with 8 mol/L NaOH solution.
- d) Attach condenser and reflux gently for 2 h.
- e) Filter the solution.

#### 16.5 Procedure—Iron Content by AA or ICP Spectrometry

Shall use manufacturers' accepted instrument settings and procedures to analyze for iron extraction sample prepared in 16.4. Iron mass concentration,  $c_{\text{Fe}}$ , in extraction filtrate, expressed in milligrams per liter shall be determined.

#### 16.6 Procedure—Iron Content by Colorimetric Determination

The following procedure shall be applied to determine iron mass concentration in filtrate by colorimetry.

- a) Transfer 10 mL of EDTA extraction filtrate from 16.4 to a 1 L volumetric flask. Record volume of filtrate as  $V$ .  
NOTE Use 1 mL of filtrate from 16.4 if the iron content is known to be high.
- b) Add ~900 mL deionized water and adjust the pH with 1 mol/L HCl to pH  $5.0 \pm 0.2$ .
- c) Dilute to volume mark (1 L) with deionized water.
- d) Measure 25 mL of solution into clean colorimeter bottle.
- e) Add contents of iron powder reagent pillow to sample. Swirl the bottle to mix. If iron is present, an orange color will develop.
- f) Let sample stand for 2 min, but no longer than 10 min before measuring the color.
- g) Fill a clean colorimeter bottle with deionized water and place it in the light cell.
- h) Insert the dedicated "Iron Meter Scale" in the spectrocolorimeter and use the dedicated color filter. Adjust the light control for a reading of 0 mg/L.
- i) Place the prepared sample [Item e) and Item f)] in the light cell and read the iron mass concentration,  $c_{\text{Fe}}$ , in milligrams per liter.

NOTE 1 Copper may interfere by forming a yellow color. One mg/L of cupric copper has been found to cause a 0.2 mg/L as iron positive error.

NOTE 2 A large excess of iron will interfere by inhibiting full color development. If there is any doubt about the validity of a given result, test a diluted sample and compare the result with the original result. Begin with a 1:1 dilution first, followed by a 9:1 dilution if the original 1:1 dilution results do not coincide.

NOTE 3 Iron reagent pillows have a limited shelf life. Under ideal (cool, dry) conditions it will keep for several years. Under poor (warm, moist) conditions, it fails after six months. Periodically perform a test on a sample containing  $\text{Fe}^{+2}$ . If no orange color develops, the iron reagent powder pillow should be discarded if the characteristic orange color develops, the pillow is still in satisfactory condition.

## 16.7 Calculation—Siderite by EDTA Extraction and AA/ICP

### 16.7.1 Siderite Mass Fraction by AA or ICP Spectrometry

The mass fraction of siderite in barite sample,  $w_{\text{FeCO}_3, \%}$ , by extraction and AA or ICP spectrometry, expressed as a percentage shall be given in Equation (28). Equation coefficients take in account extraction factor (100 mL EDTA) and weight of barite sample ( $m$ ).

$$w_{\text{FeCO}_3, \%} = 100 \times \frac{100}{1000m} \times \left( \frac{2.075 \times c_{\text{Fe}}}{1000} \right) = 2.075 \times 10^{-2} \times \left( \frac{c_{\text{Fe}}}{m} \right) \quad (28)$$

where

$c_{\text{Fe}}$  is the mass concentration of iron in extraction filtrate, expressed in milligrams per liter;  
 $m$  is the mass of the barite sample expressed in grams.

### 16.7.2 Siderite Mass Fraction by Colorimetric Determination

The mass fraction of siderite in barite sample,  $w_{\text{FeCO}_3, \%}$ , by colorimetry expressed as a percentage shall be given in Equation (29) or Equation (30), to take in account the filtrate dilution ratio used by the procedure (see 16.6).

a) Dilution of 1/100: 10 mL EDTA extraction filtrate ( $V$ ) diluted to 1000 mL:

$$w_{\text{FeCO}_3, \%} = 2.075 \times \left( \frac{c_{\text{Fe}}}{m} \right) \quad (29)$$

b) Dilution of 1/1000: 1 mL EDTA extraction filtrate ( $V$ ) diluted to 1000 mL:

$$w_{\text{FeCO}_3, \%} = 20.75 \times \left( \frac{c_{\text{Fe}}}{m} \right) \quad (30)$$

where

$c_{\text{Fe}}$  is the mass concentration of iron in extraction filtrate, expressed in milligrams per liter;  
 $m$  is the mass of the barite sample expressed in grams.

## 17 Zinc Carbonate and Lead Carbonate

### 17.1 Principle

Two of the carbonates commonly present as impurities in barite are zinc carbonate and lead carbonate. These compounds are both soluble in 10 % acetic acid, where the other common lead and zinc salts found in barite, sphalerite ( $\text{ZnS}$ ) and galena ( $\text{PbS}$ ), are not soluble in this acid.

## 17.2 Reagents, Materials, and Apparatus

17.2.1 **Acetic acid solution**, (CAS No. 64–19–7) 10 % w/w, ACS reagent grade.

17.2.2 **Oven**, regulated to 104 °C  $\pm$ 2 °C (220 °F  $\pm$ 5 °F).

17.2.3 **Desiccator**.

17.2.4 **Mortar and pestle**.

17.2.5 **Sieve**, 75  $\mu$ m (0.0029 in.-U.S sieve No. 200).

17.2.6 **Analytical balance**, with an accuracy of  $\pm$ 0.0001 g ( $\pm$ 0.1 mg).

17.2.7 **Beaker**, one 250 mL.

17.2.8 **Funnel**, one 75 mm (3 in.).

17.2.9 **Filter paper**, qualitative, standard cellulose, medium retention and filtration rate, grade 1 or equivalent, 110 mm circle (see 16.3.7).

17.2.10 **Volumetric flask**, one 100 mL.

17.2.11 **Magnetic stirrer**, with stirring bar.

17.2.12 **AA spectrophotometer** or **ICP spectrometer**, any AA or ICP unit is suitable. Instrument settings recommended by the manufacturer should be followed.

17.2.13 **AA or ICP standards, Pb and Zn**, prepared in 10 % w/w acetic acid.

## 17.3 Procedure—Acetic Acid Extraction

Extraction shall be as per the following procedure.

- Dry a representative sample of barite for 4 h in oven. Use a representative sample of barite ground such that 100 % passes through the sieve (see 17.2.5).
- Accurately weigh a 1.0 g sample of barite to 0.0001 g (0.1 mg) into the 250 mL beaker. Record sample mass, expressed in g, as *m*.
- Add 80 mL of 10 % acetic acid.
- Place stirring bar into beaker, and place beaker on stirrer. Stir for 10 min.
- Filter through filter paper into a 100 mL volumetric flask.
- Wash twice with small portions of 10 % acetic acid.
- Dilute to mark volume (100 mL) with 10 % acetic acid.

## 17.4 Procedure—Lead and Zinc Determination by AA or ICP Spectrometry

Manufacturer's accepted instrument settings and procedures to analyze for lead and zinc shall be used.

## 17.5 Calculations

Mass fractions in barite sample of zinc carbonate,  $w_{\text{ZnCO}_3, \%}$ , and lead carbonate,  $w_{\text{PbCO}_3, \%}$ , by extraction and AA or ICP spectrometry, expressed in percent shall be given respectively in Equation (31) and Equation (32). Equations take in account extraction factor (100 mL acetic acid) and weight of barite sample ( $m$ ).

$$w_{\text{ZnCO}_3, \%} = 100 \times \frac{1}{10m} \times \left( \frac{1.918 \times c_{\text{Zn-acetic ac}}}{1000} \right) = 1.918 \times 10^{-2} \times \left( \frac{c_{\text{Zn-acetic ac}}}{m} \right) \quad (31)$$

$$w_{\text{PbCO}_3, \%} = 100 \times \frac{1}{10m} \times \left( \frac{1.289 \times c_{\text{Pb-Acetic ac}}}{1000} \right) = 1.289 \times 10^{-2} \times \left( \frac{c_{\text{Pb-acetic ac}}}{m} \right) \quad (32)$$

where

- $m$  is the mass of the barite sample, expressed in grams;
- $c_{\text{Zn-acetic ac}}$  is the mass concentration of zinc in extraction filtrate (acetic acid), expressed in milligrams per liter;
- $c_{\text{Pb-acetic ac}}$  is the mass concentration of lead in extraction filtrate (acetic acid), expressed in milligrams per liter.

## 18 Total Carbonate

### 18.1 Principle

**18.1.1** Total carbonate can be released from barite by treating a sample with acid. The evolved carbonate is measured with the Garret Gas Train (GGT) and carbon dioxide ( $\text{CO}_2$ ) gas detection Dräger<sup>15</sup> tube or equivalent. The procedure is performed in an air-tight gas train with nonreactive carrier gas. The gas stream is collected in a 1 L gas bag (to allow  $\text{CO}_2$  to mix uniformly) and subsequently drawn through a Dräger tube at a fixed flowrate. The Dräger tube responds to  $\text{CO}_2$  by progressively staining purple along its length. A reaction between  $\text{CO}_2$  and a hydrazine chemical causes a crystal violet indicator to turn purple. The stain length is proportional to the total carbonate concentration in the barite sample. The barite sample appropriate to this procedure is a commercial barite of drilling fluid grade that has been ground at a mill to a size to meet fluid requirements. No further (laboratory) grinding of the sample is recommended.

### 18.2 Reagents and Materials

**18.2.1 Cylinder carrier gas**, high purity nitrogen source, with gauge and low-pressure pressure regulator.

**18.2.2 Sulfuric acid solution** (CAS No. 7664-93-9), 2.5 mol/L (5N), ACS reagent grade.

**WARNING** Sulfuric acid is a strong acid. Use proper safety precautions when handling it.

**18.2.3 Distilled or deionized water** shall be in accordance with ISO 3696 of at least Grade III.

Use deionized or distilled water for preparation of all reagents and calibration standards and as dilution water.

**18.2.4 Defoamer**, in a dropper bottle.

### 18.3 Apparatus

**18.3.1 Analytical balance**, with an accuracy of  $\pm 0.0001$  g ( $\pm 0.1$  mg).

<sup>15</sup> Dräger CO<sub>2</sub> gas detection apparatus® is an example of a suitable brand available commercially. This information is given for the convenience of users of API 13K and does not constitute and endorsement by API of these products.

**18.3.2 GGT apparatus**, consisting of a transparent plastic gas train, and inert gas supply and pressure regulator, and a Dräger tube, or equivalent shall be as described API 13B-1.

Specifications of the GGT are as follows.

a) Body

i) Chamber 1:

Depth: 90 mm (3.54 in.)

Diameter: 38 mm (1.52 in.)

ii) Chambers 2 and 3:

Depth: 90 mm (3.54 in.)

Diameter: 30 mm (1.18 in.)

iii) Passage between chambers: 2.0 mm (0.08 in.)

iv) Material: transparent material or glass that is inert to acid, sulfides, and hydrogen sulfide gas.

b) Dispersion tube

i) Stem:

Diameter: 8.0 mm (0.315 in.)

Length: 150 mm (5.9 in.)

Dispersion frit (bell-shaped, fine)

Diameter: 30 mm (1.18 in.)

Material: low coefficient of expansion, heat-resistant glass.

c) Flow meter, floating-ball type preferred, capable of measuring 300 mL/min of CO<sub>2</sub> gas.

d) Flexible tubing, type inert to hydrogen sulfide and carrier gas. Latex rubber or inert plastic tubing is preferred.

NOTE As H<sub>2</sub>S reacts with many types of rubber and plastic, use only latex rubber or inert plastic tubing.

e) Fittings and rigid tubing, type inert to hydrogen sulfide and acid.

f) Rubber septum.

**18.3.3 CO<sub>2</sub> gas detection tube:** Dräger analysis tube, marked CO<sub>2</sub>100/a (cat No. 8101811) 100 mg/L to 3000 mg/L, tube factor 2.5, or equivalent.

**18.3.4 Hypodermic syringe**, with 21-gauge needle [40 mm (1.5 in.)], one 10 mL (for acid).

**18.3.5 Magnetic stirrer**, with plastic or glass covered stirring bar, 0.6 cm × 2.5 cm (¼ in. × 1 in.).

**18.3.6 Gas bag 1 L collector:** Dräger Alcotest gas bag, No. 7626425, or equivalent.

**18.3.7 Hand-operated bellows gas-detector vacuum pump**, Dräger or equivalent.

**18.3.8 Stopcock**, 2-way bore, 8 mm (0.315 in.) glass with PTFE plug.**18.4 Procedure**

To determine total carbonate with the GGT method, the following procedure shall be applied.

- a) Ensure that the gas train is clean, dry and on a level surface, with the top removed.
  - b) Adjust the magnetic stirrer below the gas train body so that the stirring bar will freely rotate and vigorously agitate contents in Chamber 1.
  - c) Accurately weigh a 0.10 g to 0.30 g of representative barite sample to 0.0001 g (0.1 mg). Record sample mass, expressed in g, as *m*.
  - d) Transfer sample into Chamber 1.
  - e) Add 20 mL of deionized water and a few drops of defoamer.
  - f) Install the top of the gas train and hand-tighten evenly to seal O-rings.
  - f) Attach the flexible tubing from the nitrogen source to the glass dispersion tube of Chamber 1.
  - g) Adjust the dispersion tube in Chamber 1 to 20 mm  $\pm$ 3 mm (0.750 in.  $\pm$ 0.125 in.) above the bottom, just sufficient to clear the stirring bar.
  - h) Gently flow carrier gas for 1 min to purge air from the system. Check for leaks. Shut off carrier gas.
  - i) Fully collapse the gas bag and simultaneously check for leaks. To do this, connect the gas bag and stopcock to the hand pump. Open stopcock, fully depress and release the hand pump. When the gas bag is completely empty and free of leaks, the pump will remain depressed for several minutes. If leakage is detected, check the pump and all connections. To check the pump alone, insert a sealed CO<sub>2</sub> Dräger tube or equivalent, into the pump opening and depress the bellows. It will remain depressed if pump does not leak.
  - j) With the gas bag fully collapsed, install flexible tubing from the stopcock and gas bag onto the outlet of Chamber 3.
  - k) Slowly inject 10 mL of 2.5 mol/L sulfuric acid solution into Chamber 1 through the rubber septum. Use a clean syringe and needle and start rapid stirring of Chamber 1.
  - l) Open the stopcock on the gas bag. Restart the nitrogen gas flow and allow gas bag to fill steadily during a 10 min interval. When the gas bag is firm to the touch (do not burst it) shut off the nitrogen gas flow and close the stopcock. Immediately proceed to next item m).
  - m) Remove the gas bag from the gas train. Break the top off each end of CO<sub>2</sub> Dräger tube (or equivalent). Observe that an arrow on the tube indicates gas flow direction. Attach the vacuum hand pump to the downstream end of the Dräger tube (or equivalent).
  - n) Open the stopcock valve on the bag. With steady hand pressure, fully depress the hand pump. Release the pump so that the gas flows out of the bag and through the Dräger tube (or equivalent). Operate the pump and count the strokes until the bag is empty.
- NOTE Ten strokes should empty the bag. More than ten strokes indicate that leakage has occurred, and the test results will not be correct.
- o) Observe that purple/blue stain shows on the Dräger tube (or equivalent) when CO<sub>2</sub> is present in the gas bag. If the Dräger tube becomes almost filled with stain, shut off the valve and quickly replace the tube with a new one. Reopen the valve and continue the analysis.

- p) Record total stain reading from Dräger(s) tube (or equivalent),  $l_{st}$ , in units marked on the tube. Include the faint blue tinge in the purple stain length reading. If the stain reading is too low, try starting with a larger sample size. If the stain reading fills two complete tubes, repeat with a smaller sample size.

NOTE To clean the gas train, remove the flexible tubing, and remove the top. Wash with warm water and mild detergent, using a soft brush. Use a pipe cleaner to clean the passage between the chambers. Wash, rinse, and then blow out the dispersion tube with gas. Rinse the unit with deionized water and allow to drain dry.

## 18.5 Calculation

The mass concentration of total carbonate in barite sample,  $c_{CO_3\text{-tot}}$ , expressed in milligrams per kilogram shall be calculated using Equation (33).

$$c_{CO_3\text{-tot}} = \frac{(l_{st} \times f_{CO_3})}{m} = 2.5 \times \left(\frac{l_{st}}{m}\right) \quad (33)$$

where

- $m$  is the mass of the barite sample, expressed in grams;
- $l_{st}$  is the gas detection tube stain length, expressed in units marked on the tube;
- $f_{CO_3}$  is the tube factor, i.e. 2.5 for Dräger tube CO<sub>2</sub> 100/a (cat No. 8101811).

## 19 Acid-soluble Sulfides

### 19.1 Principle

**19.1.1** The concentration of acid-soluble sulfides in drilling fluid barite can be determined by acidizing with HCl and measuring the evolved hydrogen sulfide (H<sub>2</sub>S) with the GGT. The GGT separates the gas from the liquid, preventing contamination of the H<sub>2</sub>S detector.

**19.1.2** This detector is a H<sub>2</sub>S gas detection Dräger<sup>16</sup> tube or equivalent, which is the preferred detector, although a lead acetate paper disk can be accommodated in the GGT for positive or negative indication of the presence of H<sub>2</sub>S. The H<sub>2</sub>S gas indicator tube responds quantitatively to H<sub>2</sub>S by progressively darkening along its length as the H<sub>2</sub>S reacts with the reagent. The low-range Dräger tube, or equivalent is white until H<sub>2</sub>S turns it brownish black.

**19.1.3** The barite sample appropriate to this procedure is a commercial barite of drilling fluid grade that has been ground to size at a mill to meet fluid requirements. No further (laboratory) grinding of the sample is recommended because air oxidation of freshly exposed sulfide mineral surfaces will occur.

### 19.2 Reagents and Materials

**19.2.1 Cylinder carrier gas**, with gauge and low-pressure pressure regulator. Gas inert to hydrogen sulfide, acid and H<sub>2</sub>S gas detection tube reagents (Dräger or equivalent). Nitrogen should be preferred but helium is acceptable. Air nitrous oxide or other oxygen-containing gases shall be avoided.

**CAUTION** Usage nitrous oxide cartridges or air as pressure sources for GGT analysis is avoided. Under pressure, nitrous oxide or air may result in oxidation of hydrogen sulfide.

**19.2.2 Hydrochloric acid solution**, 5 mol/L (5N) (CAS No. 7647-01-0) ACS reagent grade.

<sup>16</sup> Dräger H<sub>2</sub>S gas detection tube® is an example of a suitable brand available commercially. This information is given for the convenience of users of API 13K and does not constitute and endorsement by API of these products.

**WARNING** Concentrated hydrochloric acid is a strong, potentially harmful acid. Use proper safety precautions when handling it.

**19.2.3 Defoamer**, in a dropper bottle.

**19.2.4 Deionized or distilled water** shall be in accordance with ISO 3696 of at least Grade III.

Use deionized or distilled water for preparation of all reagents and calibration standards and as dilution water.

### 19.3 Apparatus

**19.3.1 Analytical balance**, with accuracy of 0.1 g.

**19.3.2 GGT apparatus**, consisting of a transparent plastic gas train, an inert gas supply and pressure regulator, a floating-ball flow meter and a Dräger tube. See 18.3.

**19.3.3 H<sub>2</sub>S gas detection tube**: Dräger H<sub>2</sub>S analysis tubes or equivalent; low range: marked H<sub>2</sub>S 100/a (No. CH 29101) 100 to 200 H<sub>2</sub>S).

**19.3.4 Hypodermic syringe**, with 21-gauge needle [40 mm (1.5 in.)], one 20 mL for hydrochloric acid.

**19.3.5 Magnetic stirrer**, with plastic- or glass-covered stirring bar (6 mm × 25 mm (0.25 in. × 1 in.)).

### 19.4 Procedure

To determine total acid-soluble sulfides with the GGT method, the following procedure shall be applied.

a) Ensure that the gas train is clean, dry and on a level surface, with the top removed.

NOTE Moisture in the train can cause the ball in the flow meter to float erratically and can affect the accuracy of the Dräger tube (or equivalent) reading.

b) Adjust the magnetic stirrer below the gas train body so that the stirring bar will freely rotate and vigorously agitate contents of Chamber 1.

c) Nitrogen or helium shall be used as a carrier gas.

**CAUTION** Do not use nitrous oxide cartridges or air as pressure sources for GGT analysis. Under pressure, nitrous oxide or air may result in oxidation of hydrogen sulfide.

d) Weight the appropriate amount of representative barite sample to 0.1 g based on expected sulfides, using sample size suggested in Table 2. Record original sample mass, expressed in g, as *m*.

e) Transfer sample into Chamber 1.

f) Add 10 mL of deionized water and a few drops of defoamer.

g) Install the top of the gas train and hand-tighten evenly to seal O-rings.

Carefully break the tip off both ends of the H<sub>2</sub>S Dräger tube or equivalent and install the tube with the arrow pointing downward into the bored receptacle. Install the flowmeter tube with the word "Top" upward. Be sure O-ring's seal around the body of each tube. Attach the flexible tubing to the dispersion tube and to the H<sub>2</sub>S Dräger tube or equivalent.

**CAUTION** Do not clamp flexible tubing; unclamped tubing provides pressure relief in the event of over pressurization.

- h) Adjust the dispersion tube in Chamber 1 to ~20 mm  $\pm$ 3 mm (0.750 in.  $\pm$ 0.125 in.) above the bottom, just sufficient to clear the stir bar.
- i) Gently flow carrier gas for a 10-second period to purge air from the gas train. Check for leaks. Shut off carrier gas.
- j) Add 20 mL of 5 mol/L hydrochloric acid solution into Chamber 1 and start rapid stirring of Chamber 1.
- k) Immediately restart carrier gas flow. Adjust the rate between 200 mL/min and 400 mL/min. Keep floating ball in flowmeter between the two marks.
- l) Observe changes in appearance of the H<sub>2</sub>S gas detection tube (Dräger or equivalent). Record the maximum darkened length,  $l_{st}$ , in units marked on tube after flowing for a total of 60 min.

For best gas detection H<sub>2</sub>S gas detection Dräger tube (or equivalent) accuracy, the “darkened length” should fill more than half the tube's length, but less than 90 % of the total length, therefore the sample mass and gas detection Dräger tube combination shall be carefully selected. If first Dräger tube becomes almost filled with stain, shut off flow and quickly replace with a new tube. Restart the gas flow and continue the analysis. Add the two stain lengths and use the sum in the calculation.

- m) To clean the gas train, remove the flexible tubing and remove the tops. Take the Dräger tube and flowmeter out of their receptacles and plug the holes. Wash with warm water and mild detergent, using a soft brush. Use a pipe cleaner to clean the passages between chambers. Wash, rinse, and then blow out the dispersion tube with gas. Rinse the unit with deionized water and allow to drain dry.

### 19.5 Calculation

The mass concentration of acid-soluble sulfides in barite sample,  $c_s$ , expressed in milligrams per kilogram, shall be calculated using Equation (34).

$$c_s = \frac{(l_{st} \times f_s)}{m} = 0.12 \times \left(\frac{l_{st}}{m}\right) \quad (34)$$

where

- $m$  is the mass of the barite sample, expressed in grams;
- $l_{st}$  is the H<sub>2</sub>S gas detection tube Dräger maximum darkened length, expressed in units marked on the tube;
- $f_s$  is the sulfide gas detection tube factor from Table 2, i.e. 0.12.

**Table 2—H<sub>2</sub>S Dräger Tube Identification, Sample Volume, and Tube Factor to be Used for Various Sulfide Ranges**

Sulfide Range mg/Kg	Sample Mass $m$ g	Dräger Tube Identification (see tube body)	Tube Factor <sup>a</sup> $f_s$ (used in calculation)
1.2 to 24	10.0	H <sub>2</sub> S 100/a	0.12 <sup>b</sup>
2.4 to 48	5.0	H <sub>2</sub> S 100/a	0.12 <sup>b</sup>
4.8 to 96	2.5	H <sub>2</sub> S 100/a	0.12 <sup>b</sup>

<sup>a</sup> If other tubes are used, it is necessary to change the tube factor in accordance with the manufacturer's specification.

<sup>b</sup> Tube factor 0.12 applies to tubes marked H<sub>2</sub>S 100/a (Cat. No. CH 29101) with 100 to 2000 scale. For older tubes with 1 to 20 scale, use a tube factor of 12.

## 20 Calcium Hydroxide (Lime) or Cement

### 20.1 Principle

Some field samples of barite are contaminated with lime (calcium hydroxide) or cement, usually due to improper cleaning of bulk barite bins or tanks. This contamination is measured by extracting the barite sample with an aqueous solution of sucrose (sugar), which solubilizes the lime. The solution is then titrated with 0.1 mol/L (0.1N) HCl to the phenolphthalein end point. The calculation depends on whether the contaminant is known to be lime or cement. This can be known from the history of the barite or from X-ray diffraction data.

### 20.2 Reagents and Materials

**20.2.1 Sucrose** (CAS No. 57-50-1), crystalline, any granular table sugar will suffice.

**20.2.2 Hydrochloric acid solution** (CAS No. 7647-01-0) 0.1 mol/L (0.1N), ACS reagent grade.

**20.2.3 Phenolphthalein indicator** (CAS No. 77-09-8), 1 g phenolphthalein to 100 mL of 50:50 ethyl alcohol/deionized water solution.

**20.2.4 Deionized or distilled water** shall be in accordance with ISO 3696 of at least Grade III.

Use deionized or distilled water for preparation of all reagents and calibration standards and as dilution water.

### 20.3 Apparatus

**20.3.1 Sieve**, 150  $\mu\text{m}$  (0.0059 in.-U.S. sieve No.100).

**20.3.2 Analytical balance**, with an accuracy of 0.001 g (1 mg).

**20.3.3 Magnetic stirrer**.

**20.3.4 Stirring bar**.

**20.3.5 Conical flask** (Erlenmeyer), several 250 mL.

**20.3.6 Burette**, one 25 mL.

**20.3.7 Graduated cylinder** (TC), one 100 mL.

### 20.4 Procedure

The following procedure shall be applied to determine calcium hydroxide or cement in a barite sample.

- a) Use a representative barite sample ground such that 100 % passes through the sieve.
- b) Accurately weigh a 1.0 g barite sample to 0.001 g (1 mg). Record sample mass, expressed in g, as *m*.
- c) Transfer sample into the 250 mL Erlenmeyer. Add 65 mL to 75 mL deionized water and the magnetic stirring bar.
- d) Add 15.0 g  $\pm 0.1$  g sucrose (commercial crystalline sugar) and mix at medium speed on the magnetic stirrer for 1 min  $\pm 5$  s.
- e) Turn off the stirrer and let the solution stand for 2 min  $\pm 15$ s.

- f) Add 2 drops to 3 drops phenolphthalein indicator solution and titrate with 0.1N HCl to the phenolphthalein end point. Record the volume of 0.1 mol/L (0.1N) HCl required, as  $V_{\text{HCl}}$ .

## 20.5 Calculation

**20.5.1** If the contamination is thought to be only lime, the mass fraction of calcium hydroxide (lime) in barite sample,  $w_{\text{Ca(OH)}_2, \%}$ , expressed as a percentage, shall be given in Equation (35).

$$w_{\text{Ca(OH)}_2, \%} = 0.370 \times \left( \frac{V_{\text{HCl}}}{m} \right) \quad (35)$$

where

$V_{\text{HCl}}$  is the volume of 0.1 mol/L (0.1N) HCl, expressed in milliliters;

$m$  is the mass of the barite sample, expressed in grams.

**20.5.2** If the contamination is thought to be cement, the mass fraction of cement in barite sample,  $w_{\text{Cmt}, \%}$ , expressed as a percentage, shall be calculated using Equation (36).

$$w_{\text{Cmt}, \%} \cong 2 \times w_{\text{Ca(OH)}_2, \%} \quad (36)$$

where

$w_{\text{Ca(OH)}_2, \%}$  is the mass fraction of calcium hydroxide (lime) expressed as a percentage.

NOTE The value is multiplied by two as most oilfield cements are ~50 % lime.

## 21 X-ray Fluorescence Analysis

### 21.1 Principle

**21.1.1** In conventional X-ray fluorescence (XRF) spectroscopy, X-rays generated from a tube (or occasionally from radioisotopes) are used to irradiate a specimen of barite ore. This incident X-ray beam excites elements in the specimen, which then emit (fluoresce) their characteristic line X-ray spectra.

**21.1.2** These element spectra are then separated electronically or optically into individual X-ray lines, each line being characteristic of a given element.

**21.1.3** This non-destructive XRF method may be used for analysis of all elements with an atomic number greater than 10. The time for analysis is a small fraction of the time required for conventional wet chemical methods.

**21.1.4** One limitation is that analysis is for elements, not for compounds. Several rational schemes of analysis may be employed to determine mineral or compound compositions.

**21.1.5** Two basic types of XRF instruments are employed to measure spectral lines and intensities. One is wavelength dispersive XRF spectroscopy, in which the spectrum is resolved by analyzing crystals. The second instrument is energy dispersive XRF spectroscopy, which utilizes a treated silicon crystal and a multichannel analyzer to resolve energies of XRF line spectra.

**21.1.6** Since the incident X-ray beam penetrates only a few microns into the specimen surface, sample preparation is critical to obtaining good results. Both the incident (primary) X-rays and the emitted (secondary) X-rays are attenuated by the neighboring particles or atoms; this is known as a matrix effect. Thus, the physical form (e.g. particle size, surface smoothness, and element concentration) of the sample has a significant effect on the results (response) of the analysis.

**21.1.7** Two main sample preparation techniques shall be used for XRF analysis:

a) Fused Glass Disc Technique

In the fusion technique, the sample is mixed with a flux, followed by fusion at high temperature to form a stable glass bead. A major advantage of this method is that all the elements are in the same, well-defined chemical environment as a glass. The sample is homogeneous and particle size effects are eliminated. At the same time, the sample is diluted with flux, so matrix effects are small and can be accurately resolved.

b) Pressed Powder Technique

In the pressed powder technique, the barite powder (either neat or mixed with a small amount of binder) is pressed under high pressure into a pellet, which is then analyzed by XRF spectroscopy. This method is much faster and simpler than the fusion technique, but less accurate however, if carefully performed this technique can be reasonably accurate. Analysis of the lower atomic number elements such as aluminum and silicon are less accurate. This procedure also requires an extensive library of standard samples analyzed by wet chemical techniques and consisting of elements in matrix material similar to the sample.

## 21.2 Reagents and Materials

**21.2.1 Lithium tetraborate** (CAS NO. 12007-60-2), anhydrous, "spectral" grade powder.

**21.2.2 Boric acid** (CAS No. 10043-35-3), "spectral" grade powder.

**21.2.3 Germanium oxide** (CAS No. 20619-16-3), "spectral" grade powder.

**21.2.4 Lithium carbonate** (CAS No. 584-13-2), anhydrous, "spectral" grade powder.

**21.2.5 Lithium nitrate** (CAS No. 7790-69-4), anhydrous, "spectral" grade powder.

**21.2.6 Lanthanum oxide** (CAS No. 1312-81-8), "spectral" grade powder.

**21.2.7 Hydrobromic acid solution** (10 %), (CAS No. 10035-10-6) 10 g HBr to 90 mL deionized water.

**21.2.8 Flux mixture A**, 47 % lithium tetraborate (CAS No.12007-60-2), 37 % lithium carbonate (CAS No.554-13-2) 16 % lanthanum oxide (CAS No. 1312-81-8).

**21.2.9 Flux mixture B**, 90 % lithium tetraborate (CAS No.12007-60-2), 10 % lithium nitrate (CAS No.7790-69-4).

**21.2.10 Synthetic standards**, several made from "pure" element compounds, such as  $\text{BaSO}_4$ ,  $\text{SrSO}_4$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and others, to cover all elements being analyzed. The range of concentrations should cover the anticipated ranges in the unknowns.

**21.2.11 Barite ore standards**, several, all analyzed by conventional wet chemical techniques. Again, the concentration ranges of  $\text{BaSO}_4$ ,  $\text{SrSO}_4$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and others, should cover anticipated levels of the unknowns.

## 21.3 Apparatus

**21.3.1 X-ray fluorescence spectrometer**, any XRF unit is suitable. Instrument settings recommended by the manufacturer should be followed.

**21.3.2 Computer software for XRF spectrometer** (usually supplied by spectrometer manufacturer), optional.

**21.3.3 Muffle furnace**, regulated to  $1100\text{ }^\circ\text{C} \pm 20\text{ }^\circ\text{C}$  ( $2010\text{ }^\circ\text{F} \pm 35\text{ }^\circ\text{F}$ ).

**21.3.4 Drying oven**, regulated to  $110\text{ }^\circ\text{C} \pm 5\text{ }^\circ\text{C}$  ( $230\text{ }^\circ\text{F} \pm 10\text{ }^\circ\text{F}$ ).

**21.3.5 Meker-type burner**, two or more, capable of producing heating up to 120 °C (250 °F).

**21.3.6 Crucibles and covers**, 95 % platinum–5 % gold, several 20 mL to 25 mL.

NOTE Graphite crucibles may also be used as an alternative.

**21.3.7 Molds**, 95 % platinum–5 % gold, several sized to fit XRF sample holder.

NOTE Graphite molds may also be used as an alternative.

**21.3.8 Hydraulic pellet press**, capable of pressures of at least 276,000 kPa (40,000 lbf/in.<sup>2</sup>).

**21.3.9 Pellet press die**, sized to fit XRF sample holder.

**21.3.10 Impact grinder and grinding vials.**

**21.3.11 Timer**, accurate at  $\pm 5$  s per hour.

**21.3.12 Hot plate.**

**21.3.13 Analytical balance**, with accuracy of 0.001 g (1 mg).

**21.3.14 Sieve**, 45  $\mu\text{m}$  (0.0018 in.-U.S. sieve No. 325).

**21.3.15 Crucible tongs.**

**21.3.16 Stirring rod**, PTFE, or plastic equivalent.

**21.3.17 Sample cups**, polyethylene terephthalate (PET) or plastic equivalent, sized to fit XRF sample holder.

**21.3.18 Plastic sealing film**, polyvinylidene chloride (PVDC) or equivalent, to seal sample cups.

## **21.4 XRF Analysis—Procedures**

### **21.4.1 Barite Sample Preparation**

Barite samples shall be prepared as per the following procedure.

- a) Dry a representative sample of barite for at least 2 h at 110 °C (230 °F).
- b) Grind the dried sample in the impact grinder such that 100 % passes through the 45  $\mu\text{m}$  sieve. This is the dried sample.
- c) Place part of the ground sample in a platinum-gold or graphite crucible and ash in the muffle furnace for 30 min at 1000 °C  $\pm 20$  °C (1830 °F  $\pm 35$  °F).

**WARNING** Use proper safety precautions when handling hot crucible and melt.

- d) Grind the ashed sample in the impact grinder to 100 % passes through the 45  $\mu\text{m}$  sieve. This is the ashed sample.
- e) One or more of the following methods of sample preparation (21.4.2 through 21.4.5) may be used.

### **21.4.2 Procedure—Fused Glass Disc Technique with Flux A**

For XRF analysis method using fused glass disc technique and flux A, the following procedure shall be applied.

- a) Accurately weigh on the analytical balance 0.500 g  $\pm$ 0.001 g ground, ashed barite [preparation described under 21.4.1, Item d)] with 0.050 g  $\pm$ 0.005 g germanium oxide and 2.00 g  $\pm$ 0.05 g flux mixture A into a platinum-gold crucible.
- b) Mix with PTFE rod.
- c) Fuse in the muffle furnace for 15 min at 980 °C  $\pm$ 20 °C (1800 °F  $\pm$ 35 °C). Swirl melt, using the crucible tongs, to ensure mixing of products after 5 min.

**WARNING** Use proper safety precautions when handling hot crucible and melt.

- d) Pour the melt into the platinum-gold mold that is kept at  $\sim$ 220 °C (425 °F) on the hot plate.
- e) Allow the temperature of the melt to moderate for  $\sim$ 10 min. the melt bead should shrink with cooling and pop free of the mold.
- f) Using tongs separate the bead from the mold and place the bead on an unglazed tile.
- g) As the bead cools, it should easily pop free of the mold. This bead may be analyzed as is (using the bottom surface for analysis) or further polished before XRF analysis.
- h) Prepare several standards (synthetic and/or analyzed barite standards) in the same manner.

#### 21.4.3 Procedure—Fused Glass Disc Technique with Flux B

For XRF analysis method using fused glass disc technique and flux B, the following procedure shall be applied.

- a) Accurately weigh on the analytical balance 1.000 g  $\pm$ 0.001 g ground, ashed barite [preparation described under 21.4.1, Item d)] with 4.350 g  $\pm$ 0.001 g flux mixture B into a platinum-gold crucible.
- b) Mix with PTFE rod.
- c) Add 10 drops of 10 % HBr solution to the mixture and cover the crucible.
- d) Place the crucible over a Meker-type burner and heat on low flame for a few minutes.
- e) Increase the flame and fuse the samples for 8 min at high temperature, which is above 1000 °C (1830 °F).
- f) Swirl the crucible occasionally, using the crucible tongs, to aid in forming a homogeneous melt and to assist the release of any gas phase that may form during fusion.

**WARNING** Use proper safety precautions when handling hot crucible and melt.

- g) Place the platinum-gold mold over a second Meker-type burner and heat to high temperature.
- h) When the fused melt is clear and free of bubbles, pour into the heated mold.
- i) Place the filled mold on a piece of unglazed tile and allow it to cool.
- j) As the glass bead cools, it will pop free of the mold. This bead may be analyzed as is (using the bottom surface for analysis) or further polished before XRF analysis.

#### 21.4.4 Procedure—Fusion/Pressed Disc Technique

For XRF analysis method using fusion/pressed disc technique, the following procedure shall be applied.

- a) Accurately weigh on the analytical balance 0.500 g  $\pm$ 0.001 g representative barite sample [ground, ashed barite preparation, see 21.4.1 item d)] and 1.00 g  $\pm$ 0.05 g lithium tetraborate into a platinum-gold crucible.

NOTE Depending upon balance capacity of if tare cannot be maintained it may be necessary to pre-weigh the empty crucible and record mass of the crucible  $\pm$ 0.001 g.

- b) Mix with PTFE rod.
- c) Place into muffle furnace and fuse for 15 min at 1050 °C to 1100 °C (1925 °F to 2010 °F) with occasional swirling of the melt to ensure thorough mixing.

**WARNING Use proper safety precautions when handling hot crucible and melt.**

- d) Cool melt bead in the crucible and add boric acid to total weight of bead and boric 1.600 g  $\pm$ 0.001 g.

NOTE Crucible weigh must be considered if balance Tare could not be sustained.

- e) Grind the mixture for 10 min in the impact grinder.
- f) Press in the hydraulic press at 276,000 kPa (40,000 lbf/in.<sup>2</sup>) using boric acid as backing to the disc.
- g) Repeat with several synthetic and/or analyzed standards.

#### 21.4.5 Procedure—Pressed Powder Technique

For pressed powder XRF analysis the following procedure shall be applied.

- a) Place in standard die a 20 g dried and ground (but not ashed) sample [see 21.4.1, Item a) and Item b)] and press to 276,000 kPa (40,000 lbf/in.<sup>2</sup>) with a hydraulic press. The resulting pellet is saved for XRF analysis.

NOTE As an alternative procedure, the loose barite powder may be placed in a plastic sample cup, using a plastic sealing film (PVDC or equivalent) to hold the sample and to act as a “window” to incident X-ray beam. The accuracy and precision of this method, however, are not as high as for the pressed pellet procedure.

- b) Several standards (both synthetic and analyzed standards may be used) are prepared in the same manner [see 21.4.5, Item a)].
- c) If the pellet does not hold together after it is made, a small amount (e.g. 10 %) of a binder such as boric acid may be added to the sample, mixed thoroughly, and pressed into a pellet. If this is done, then the standards must be prepared in the same manner.

#### 21.5 Procedure—Spectral Analysis

**21.5.1** Using the instrument settings recommended by the manufacturer, spectra of the elements of interest for both standards and unknown barite samples shall be collected.

NOTE Eight elements are routinely analyzed: barium iron, silicon, aluminum, calcium, sulfur, strontium, and magnesium. Other “minor” elements such as lead, zinc, manganese, potassium, etc., can also be analyzed, but are usually present at low or trace concentrations.

**21.5.2** Spectral data shall be collected long enough for adequate precision in the results. This can usually be determined by following instructions that come with the instrument or the computer software.

**21.5.3** Most instrument manufacturers should provide computer software that accomplishes data manipulation automatically. This includes storage of standard spectra, linear and nonlinear regression analysis, statistical analysis, and matrix correction programs.

## 21.6 Calculation

### 21.6.1 Fused Glass Disc Technique

There is little or no inter-element or matrix correction. The flux A method contains lanthanum ion; this effectively dilutes the sample to a level where the concentration/X-ray intensity relationship is linear. The analysis shall be compared with calibrated standards, either graphically or by computer software.

For both fusion methods, the concentrations of elements obtained from XRF analysis,  $w_{\text{Elmt-ash barite, \%}}$  are for ashed samples, not for as-received samples (see 21.4.1). To correct for element concentration in the barite sample, the correction for *LOI*, shall be applied. Mass fraction of an element in barite sample (as received),  $w_{\text{Elmt-barite, \%}}$ , expressed as a percentage, shall be calculated using Equation (37).

$$w_{\text{Elmt-barite, \%}} = \frac{w_{\text{Elmt-ash barite, \%}} \times (100 - \text{LOI})}{100} \quad (37)$$

where

$w_{\text{Elmt-ash barite, \%}}$  is the mass fraction of element in ashed barite sample, expressed as a percentage;

*LOI* is the loss of ignition of barite sample, expressed as a percentage.

### 21.6.2 Fusion/Pressed Disc Technique

The results shall be compared with standards and fitted to curves drawn from concentration/intensity values. The concentration/X-ray response is nonlinear and is corrected from the calibration curves.

For fused glass disc technique, the concentrations of elements obtained from XRF analysis,  $w_{\text{Elmt-ash barite, \%}}$  are for ashed samples, not for as-received samples (see 21.4.1). To correct for element concentration in the barite sample, the correction for *LOI*, shall be applied. Mass fraction of an element in barite sample (as received),  $w_{\text{Elmt-barite, \%}}$ , expressed as a percentage, shall be calculated using Equation (37), (see 21.6.1).

### 21.6.3 Pressed Powder Technique

In this method the matrix effects are large, and consequently many analyzed samples must be examined to obtain accurate and reproducible results. Calibration curves will be nonlinear, but computer programs can be used for both nonlinear regression analysis and to correct for matrix effects.

## 22 Mercury in Drilling Fluid Barite

### 22.1 Principle

**22.1.1** This method covers the determination of mercury (Hg) in drilling fluid barite. The cold-vapor AA technique is used for the analysis, following sample digestion and oxidation to ensure that most of the Hg in the sample is dissolved in the aqueous medium and converted to the mercuric ion.

**22.1.2** The cold-vapor AA technique is based on the absorption of light energy at 253.7 nm by Hg vapor. Hg is reduced to the elemental state and purged from solution in a closed system. The Hg vapor passes through a cell positioned in the light path of an Hg source lamp. Absorbance (peak height) is measured as a function of Hg content.

### 22.2 Reagents and Materials

**WARNING** Concentrated acids (hydrochloric, nitric, and aqua regia) are strong, potentially harmful acids. Use proper safety precautions when handling them.

**22.2.1 Deionized or distilled water** shall be in accordance with ISO 3696 Grade II requirements.

Distilled or deionized water grade II shall be used for preparation of all reagents and calibration standards and as dilution water.

NOTE Special reagents low in Hg are available for the chemicals described in 22.2.2 to 22.2.7.

**22.2.2 Hydrochloric acid concentrated** (CAS No. 7647-01-0), 37 % w/w, ACS reagent grade.

**22.2.3 Nitric acid concentrated** (CAS No. 7697-37-2), 70 % w/w, ACS reagent grade.

**22.2.4 Aqua regia** (CAS No. 8007-56-5). Prepared immediately before use by carefully adding three volumes of concentrated hydrochloric acid (37 % w/w HCl) to one volume of concentrated nitric acid (70 % w/w HNO<sub>3</sub>).

**22.2.5 Hydrochloric acid solution 1.2 mol/L (1.2 N)** (CAS No. 7647-01-0).

**22.2.6 Stannous chloride solution** (CAS No. 7772-99-8), add 10 g ±0.1 g stannous chloride (SnCl<sub>2</sub>) (ACS reagent grade) to 50 mL of 1.2 mol/L HCl in a 100 mL volumetric flask. Dilute to volume with 1.2 mol/L hydrochloric acid.

**22.2.7 Hydroxylamine hydrochloride 12 % solution** (CAS No. 5470-11-1). Dissolve 12 g of hydroxylamine hydrochloride (NH<sub>2</sub>OH•HCl) in deionized water grade II and dilute to 100 mL with deionized water grade II.

**22.2.8 Potassium permanganate 5 % solution**, mercury free (CAS No. 7722-64-7). Dissolve 5 g of potassium permanganate (KMnO<sub>4</sub>) in 100 mL of deionized water grade II.

**22.2.9 Potassium persulfate solution** (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>), ACS reagent grade (CAS No. 7727-21-1). Dissolve 50 g K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in pure water and dilute to 1 L with hot [60 °C (140 °F)] deionized water grade II.

**22.2.10 Mercury, stock solution** (1 mL solution ≡ 1 mg Hg, which is equivalent to a 1 g/L Hg standard).

Dissolve 0.1354 g ±0.0001 g (±0.1 mg) of mercuric chloride in 75 mL of deionized water grade II. Add 10 mL of concentrated HNO<sub>3</sub> 37 % w/w and adjust the volume to 100 mL.

NOTE Commercial Hg stock solutions are available and can be used as an alternative to preparing the stock solution.

**22.2.11 Mercury, intermediate solution** (1 mL solution ≡ 10 µg Hg, which is equivalent to a 10 µg/mL or 10 mg/L Hg standard).

Pipette 1 mL Hg stock solution into a 100 mL volumetric flask and bring to volume with deionized water grade II containing 10 mL concentrated 70 % HNO<sub>3</sub> per liter. Solution is expected to be stable for several weeks. Lower-concentration Hg standards (< 10 µg/mL) should be stored in glass to avoid losses/gains of Hg by exchange with the atmosphere.

**22.2.12 Mercury, working solution** (1 mL solution ≡ 0.1 µg Hg, which is equivalent to 0.1 µg/mL or 0.1 mg/L Hg standard).

Pipette 1 mL of the Hg intermediate solution into a 100 mL volumetric flask and bring to volume with deionized water grade II containing 10 mL concentrated HNO<sub>3</sub> 37 %w/w per liter.

**22.2.13 Potassium permanganate 10 % solution**, (CAS No. 7722-64-7). Dissolve 100 g of potassium permanganate (KMnO<sub>4</sub>) per liter of solution.

**22.2.14 Sulfuric acid 10 % solution** (CAS No. 7664-93-9).

**22.2.15 Potassium permanganate 0.02 mol/L (0.1N)** (CAS No. 7722-64-7). Dissolve 3.16 g of potassium permanganate (KMnO<sub>4</sub>) per liter of solution.

## 22.3 Apparatus

### 22.3.1 AA Spectrophotometer

Any AA unit equipped with background compensation and having an open sample presentation area in which to mount the absorption cell is suitable. Recommendations for instrument settings by the manufacturer should be followed.

Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the AA spectrophotometer (see OSPAR Commission Publication [3]).

### 22.3.2 Mercury hollow-cathode or electrode-discharge lamp.

### 22.3.3 Recorder

Any multi-range, variable-speed recorder compatible with the ultraviolet detection system is suitable.

**22.3.4 Absorption cell.** Standard spectrophotometer cells 100 mm (4.0 in.) long having quartz end windows may be used. The cell is attached to a burner for support and aligned in the light beam to give maximum transmittance.

NOTE 1 Suitable cells can be constructed from glass tubing with dimensions approximately of diameter 25 mm (1.0 in.) × 100 mm (4.0 in.) length with quartz windows 25 mm (1.0 in.) in diameter × 6 mm (0.25 in.) thickness cemented in place at the ends. Gas inlet and outlet ports [also of glass but 8 mm (0.3125 in.) diameter] are attached ~13 mm (0.625 in.) from each end.

NOTE 2 Longer cells [e.g. 300 mm (12.0 in.)] are common to separable Hg systems and provide lower detection limits.

**22.3.5 Gas source,** nitrogen, or argon.

**22.3.6 Flowmeter,** capable of measuring a gas flow rate of ~1 L/min.

**22.3.7 Aerator** comprised of a straight glass frit having a coarse porosity. Clear flexible plastic tubing is used for passage of the Hg vapor from the sample bottle to the absorption cell and return.

**22.3.8 Drying tube,** of diameter 150 mm (6 in.) × 19 mm (<sup>3</sup>/<sub>4</sub> in.), containing 20 g of magnesium perchlorate with glass wool packed at each end.

**22.3.9 Reaction bottle,** 250 mL to 300 mL glass container, fitted with ground glass joint. A gas-washing bottle best serves as a reaction bottle.

**22.3.10 Digestion vessel,** 250 mL flask with a ground-glass joint fitted with a water-cooled condenser.

**22.3.11 Filtration cell,** any apparatus capable of filtering the digested sample

**22.3.12 Filter paper,** quantitative, ashless, medium filtration rate, grade 40 (see 5.3.13), or grade 42, (see 9.3.6), or equivalent, circle 110 mm (4.3 in.).

**22.3.13 Analytical balance,** with accuracy of 0.0001 g (0.1 mg).

## 22.4 Preparation of Standards

NOTE Some mercury test apparatus require standards with mass concentrations 10 times higher.

#### 22.4.1 Hg standard, 0.005 µg/mL

Place 5 mL of Hg working solution (see 22.2.12) in a 100 mL volumetric flask and dilute to the mark with 1.2 mol/L HCl.

#### 22.4.2 Hg standard, 0.01 µg/mL

Place 10 mL of Hg working solution in a 100 mL volumetric flask and dilute as in 22.4.1.

#### 22.4.3 Hg standard, 0.02 µg/mL

Place 20 mL of Hg working solution in a 100 mL volumetric flask and dilute as in 22.4.1.

#### 22.4.4 Hg standard, 0.05 µg/mL

Place 50 mL of Hg working solution in a 100 mL volumetric flask and dilute as in 22.4.1.

### 22.5 Sample Digestion

To prepare the digested volume,  $V_0$ , of barite sample, the following procedure shall be applied.

- Weigh a 2.0 g representative barite sample to 0.0001 g (0.1 mg), record sample mass expressed in g, as  $m$  and place in the 250 mL digestion flask.
- Add 40 mL aqua regia, 15 mL  $\text{KMnO}_4$  5 % solution, and 8 mL  $\text{K}_2\text{S}_2\text{O}_8$  solution to the flask and reflux for approximately 1 h using a water-cooled condenser in a fume hood. Cool.

**CAUTION** Take extreme care to prevent loss of mercury during the digestion [Item b)].

- Add 6 mL of the hydroxylamine hydrochloride solution to reduce excess permanganate as evidenced by a loss of color.
- Allow solids to settle and filter through filter paper into a 100 mL volumetric flask. Wash the digestion flask and residue several times onto the filter with deionized water grade II. Dilute to  $V_0$  volume (100 mL volume-mark) with deionized water grade II.
- Prepare a procedural blank by carrying out 22.5 Item b) through Item d) without a sample.

### 22.6 Recovery of Hg during Digestion—Check

Procedure to check for HG recovery shall be as per the following.

- Transfer a 10 mL aliquot of the working solution (see 22.2.12), containing 1.0 µg Hg, to one of the 250 mL digestion flasks.
- Treat as in 22.5 Item b) through Item d).

### 22.7 Standards and Samples—Analysis

Procedure to analyze standards and samples shall be as per the following.

**WARNING** Mercury vapor is toxic, use safety precautions to avoid its inhalation.

- Analysis system shall include a trap in it to pass the mercury vapor through an absorbing medium, such as equal volumes of 0.02 mol/L  $\text{KMnO}_4$  and 10 %  $\text{H}_2\text{SO}_4$  solutions. Examples of analytical systems with a trap can be found in US EPA Method 245.1, Revision 3, Figure 1.

- b) Switch on the Hg system. Adjust airflow and zero instrument according to manufacturer's specifications.

NOTE Each Hg analysis system has a slightly different physical arrangement and methodology. The system discussed below serves as one useful example of a single-pass arrangement.

- c) Place 5 mL of stannous chloride solution in a reaction bottle containing 100 mL deionized water grade II and allow purge gas to pass through the aeration apparatus and the absorption cell until no absorbance signal is observed.
- d) Divert gas flow with a two-way valve and place 1 mL of the 0.005 µg/mL Hg standard (22.4.1) in the reaction bottle, wait 1 min, and then let purge gas run until a peak is observed on the recorder and the signal subsequently returns to zero. Rinse flask with 1.2 mol/L (1.2 N) HCl and then deionized water grade II between analyses. Repeat with each standard prepared in 22.4.2 through 22.4.4.

NOTE With some Hg systems, adjust airflow and zero instrument according to the manufacturer's specification.

- e) Repeat Item c) through Item d) for each sample, using 0.5 mL to 5 mL aliquots (from the 100 mL total). Record aliquot volumes as  $V_s$ .

NOTE With some Hg systems, the standard curve can use 0.05 µg, 0.1 µg, 0.2 µg, 0.5 µg and 1.0 µg Hg values.

- f) Also analyze 1 mL of the sample prepared for Hg recovery check in 22.6. Absorbance for that sample shall be at least 95 % of that for the 0.010 µg/mL Hg standard (see 22.4.2).

## 22.8 Calculation

**22.8.1** Following analysis of the standards, a standard curve by plotting peak height versus micrograms of mercury (0 µg, 0.005 µg, 0.01 µg, 0.02 µg, 0.05 µg, 0.10 µg) shall be constructed.

NOTE With some Hg systems, the standard curve can use 0.05 µg, 0.1 µg, 0.2 µg, 0.5 µg and 1.0 µg Hg values.

**22.8.2** Measuring the peak height of the test sample its mercury value ( $m_{\text{Hg}}$ ) shall be determined from the standard curve.

**22.8.3** Mercury mass concentration in barite sample,  $c_{\text{Hg}}$ , expressed in milligrams per kilogram, shall be given in Equation (38).

$$c_{\text{Hg}} = \frac{m_{\text{Hg}}}{V_s} \times \frac{V_o}{m} = m_{\text{Hg}} \times \left( \frac{V_o}{m V_s} \right) \quad (38)$$

where

$m_{\text{Hg}}$  is the mass of mercury in the digested sample, expressed in micrograms;

$m$  is the mass of original barite sample, expressed in grams;

$V_o$  is the volume of barite digested solution, expressed in milliliters (100 mL in this procedure);

$V_s$  is the sample aliquot, expressed in milliliters.

NOTE One milligram per kilogram is equivalent to one microgram per gram.

## 23 Cadmium and Lead in Drilling Fluid Barite

### 23.1 Principle

**23.1.1** This method covers the determination of cadmium (Cd) and lead (Pb) in drilling fluid barite. Atomic absorption (AA) is used for analysis, following sample digestion, to ensure that most of the Cd and Pb in the sample dissolve in the aqueous medium.

**23.1.2** The aqueous sample containing the dissolved Cd and Pb ions is atomized and aspirated into a flame. During separate analyses, light beams of wavelength 228.8 nm for Cd and 283.3 nm for Pb are passed through the flame into a monochromator and onto a detector that measures the amount of light absorbed. The light energy absorbed in the flame is a measure of the concentrations of Cd and Pb in the sample.

### 23.2 Reagents and Apparatus

**WARNING** Concentrated acids (hydrochloric and nitric) are strong, potentially harmful acids. Use proper safety precautions when handling them.

**23.2.1 Distilled or Deionized water** shall be in accordance with ISO 3696 Grade II requirements.

Use distilled or deionized water grade II shall be used for the preparation of all reagents and calibration standards and as dilution water.

**23.2.2 Hydrochloric acid diluted solution** (1:1), (CAS No. 7647-01-0), ACS reagent grade.

**23.2.3 Nitric acid** ( $\text{HNO}_3$ ) (CAS No. 7697-37-2) concentrated 70 % w/w, ACS reagent grade.

**23.2.4 Cadmium nitrate** (CAS No. 10022-68-1), for Cd stock solution (1 mL solution  $\equiv$  0.1 mg Cd, which is equivalent to a 100  $\mu\text{g}/\text{mL}$  or 100 mg/L standard).

Weigh 0.2744 g  $\pm$  0.0001 g ( $\pm$  0.1 mg) of cadmium nitrate [ $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , analytical reagent grade], dissolve in 200 mL deionized water grade II in a 1 L volumetric flask. Add 20 mL hydrochloric acid solution 1:1 and dilute to volume mark with deionized water grade II.

**23.2.5 Lead nitrate** (CAS No. 100997-4-8), for Pb stock solution (1 mL solution  $\equiv$  1 mg Pb, which is equivalent to a 1 mg/mL or 1 g/L standard).

Weigh 1.599 g  $\pm$  0.0001 g ( $\pm$  0.1 mg) of lead nitrate [ $\text{Pb}(\text{NO}_3)_2$ , analytical reagent grade], dissolve in 200 mL of deionized water grade II, add 10 mL concentrated  $\text{HNO}_3$  70 % w/w (23.2.3) and dilute to 1 L with deionized water grade II.

**NOTE** Commercial Cd and Pb stock solutions are available and recommended as an alternative to preparing the stock solution. For Cd, the 100  $\mu\text{g}/\text{mL}$  stock solution (23.2.4) can be prepared by placing 100 mL of the 1  $\mu\text{g}/\text{L}$  standard in a 1 L volumetric flask, adding 20 mL of hydrochloric acid (23.2.2) and diluting to the volume mark with deionized water grade II.

**23.2.6 Analytical balance**, with an accuracy of 0.0001 g (0.1mg).

#### 23.2.7 AA Spectrophotometer

Any commercial AA unit having an energy source, an atomizer burner system, a monochromator, a detector, and background compensation is suitable. Recommendations for instrument settings by the manufacturer should be followed.

**23.2.8 Cadmium and lead hollow-cathode or electrodeless discharge lamps.**

**23.2.9 Fuel**, commercial grade acetylene is generally acceptable.

**23.2.10 Oxidation air**, supplied from a compressed-air line, a laboratory compressor or from a cylinder of compressed air.

**23.2.11 Digestion flask**, of capacity 250 mL, with a ground-glass joint, fitted with a water-cooled condenser.

**23.2.12 Filtration cell**, any apparatus capable of filtering the digested sample through filter paper.

**23.2.13 Filter Paper**, quantitative, ash-less, medium filtration rate, grade 40 (see 5.3.13), or grade 42 (see 9.3.6) or equivalent, circle 110 mm.

### 23.3 Preparation of Combined Cadmium and Lead Standards

#### 23.3.1 Standard, 0.1 µg/mL Cd + 1 µg/mL Pb

Transfer 1 mL aliquots each of the Cd and the Pb stock solutions to a 1 L volumetric flask, fill about half-full with deionized water grade II, add 10 mL HCl solution 1:1 and dilute with deionized water grade II to 1 L. Store in acid-washed plastic bottles.

#### 23.3.2 Standard, 0.2 µg/mL Cd + 2 µg/mL Pb

Use 2 mL aliquots of each stock solution and repeat dilution as in 23.3.1.

#### 23.3.3 Standard, 0.5 µg/mL Cd + 5 µg/mL Pb

Use 5 mL aliquots of each stock solution and repeat dilution as in 23.3.1.

#### 23.3.4 Standard, 1 µg/mL Cd + 10 µg/mL Pb:

Use 10 mL aliquots of each stock solution and repeat dilution as in 23.3.1.

#### 23.3.5 Standard, 2 µg/mL Cd + 20 µg/mL Pb

Use 20 mL aliquots of each stock solution and repeat dilution as in 23.3.1.

NOTE All standards should be stored in polyethylene bottles and it is expected that they are stable for several months.

#### 23.3.6 Procedural Blank

Prepare an acid blank by using the same procedure as shown in 23.3.1 without adding Cd or Pb stock solution.

### 23.4 Sample Acid Digestion

To prepare digested volume,  $V_0$ , of the barite sample, the following procedure shall be applied.

- a) Weigh a 10.0 g or a smaller representative barite sample to 0.0001 g (0.1 mg). Record sample mass, expressed in g, as  $m$ . Place in the 250 mL flask.
- b) Add 50 mL hydrochloric acid (23.2.2) to the flask and reflux for 1 h using the water-cooled condenser.
- c) Allow flask and contents to cool.
- d) Let solids settle and decant through a filter paper grade 40 or grade 42, into a 100 mL volumetric flask. Wash residue and digestion flask with deionized water grade II, let settle and decant through filter. Dilute to  $V_0$  volume (100 mL volume mark) with deionized water grade II. Aliquots of the well-mixed, filtered digest solution may be stored in smaller plastic containers for several weeks.

- e) Prepare a procedural blank by performing digestion procedure Item a) through Item d) without sample.

NOTE No losses of Cd or Pb were found during acid digestion.

### 23.5 Analysis of Standards and Samples

Analyze of standards and samples for cadmium and lead shall be as per the following procedure.

NOTE 1 One alternative procedure for determining Cd or Pb in the extract is the use of a graphite furnace, or flameless AA spectrophotometry. In this process, a heated graphite tube rapidly volatilizes the Cd- or Pb-containing solution; the vapor thus generated is analyzed for the Cd or Pb content using an AA spectrophotometer.

NOTE 2 A second alternative method for determining Cd or Pb in the digest solution is the use of a plasma spectrophotometer, available as either DCP (direct current plasma) or ICP. These instruments aspirate the extract into a plasma where the solution is volatilized. The Cd or Pb atoms thus generated are excited to a high energy level by the plasma and then emit radiation that is characteristic of the atomic structure of Cd or Pb. This radiation is then separated from other radiation emitted by a monochromator and is measured quantitatively by a photomultiplier.

- Switch on the AA instrument and configure it for flame atomization for Cd at 228.8 nm according to the manufacturer's instructions.
- Aspirate each of the Cd/Pb standards (see 23.3.1 through 23.3.5) into the instrument and record the absorbance and Cd concentration of each standard. Repeat until each of the standards gives a uniform absorbance. Aspirate deionized water grade II between the analyses of each different standard.
- Proceed with the aspiration of acid blank (see 23.3.6), procedural blanks [see 23.4, Item e)] and samples, recording the absorbances and again aspirating deionized water grade II between analyses of each sample.
- Re-run the standards after every 6–10 samples and at the conclusion of the sample set.
- Configure the instrument for flame atomization for Pb at 283.3 nm according to the manufacturer's instructions and repeat Item a) through Item d) for analysis of Pb.

### 23.6 Calculation

**23.6.1** A separate calibration curve for Cd and for Pb shall be prepared by plotting the absorbance versus mass concentration for each standard.

**23.6.2** Using the sample absorbance and the Cd and Pb calibration curves from 23.6.1, separately, the digest solution Cd and Pb mass concentrations,  $c_{Cd}$  and  $c_{Pb}$ , shall be determined by subtracting any procedural blank (which is expected to be essentially zero).

**23.6.3** Cadmium and lead mass concentrations in barite sample,  $c_{Cd}$  and  $c_{Pb}$ , expressed in milligrams per kilogram of barite sample, shall be given in Equation (39) and Equation (40).

$$c_{Cd} = c_{Cd-hydchlor\ ac} \times \left( \frac{V_o}{m} \right) \quad (39)$$

$$c_{Pb} = c_{Pb-hydchlor\ ac} \times \left( \frac{V_o}{m} \right) \quad (40)$$

where

$c_{Cd-hydchlor\ ac}$  is the mass concentration of cadmium in the acid digested sample (HCl), expressed in micrograms per milliliter;

- $C_{\text{Pb-hydchlor ac}}$  is the mass concentration of lead in the acid digested sample (HCl), expressed in micrograms per milliliter;
- $V_o$  is the volume of digested solution, expressed in milliliters (100 mL in this procedure);
- $m$  is the mass of barite sample, expressed in grams.

NOTE One milligram per kilogram is equivalent to one microgram per gram.

## 24 Arsenic in Barite

### 24.1 Principle

**24.1.1** This method covers the determination of arsenic (As) in drilling fluid barite. The gaseous hydride AA method is used for analysis, following sample digestion and reduction to ensure that most of the As in the sample is dissolved in the aqueous medium and converted to the trivalent form.

**24.1.2** The gaseous hydride method is based on the absorption of light energy at 193.7 nm by As. Arsenic in the trivalent form is converted to gaseous arsine ( $\text{AsH}_3$ ) using sodium borohydride ( $\text{NaBH}_4$ ) in an acid medium. The gaseous hydride is swept through a heated quartz tube or into the argon/hydrogen flame of an AA spectrophotometer. The As concentration is determined as a function of the measured absorbance (peak height).

NOTE An alternative procedure for determining As in the extract is the use of flameless AA spectrophotometry. In this process, a heated graphite tube rapidly volatilizes the As-containing solution; the vapor thus generated is measured for As, using an AA spectrophotometer. This method of analysis eliminates the need for the arsine generator and is also more sensitive to As. Graphite furnaces are commercially available from most manufacturers of AA instruments. The manufacturer's recommendations for instrument settings for As should be followed. However, slight modifications in these settings can be needed to optimize the sensitivity and reproducibility of the As analysis.

### 24.2 Reagents and Apparatus

**24.2.1 Distilled or deionized water** shall be in accordance with ISO 3696 Grade II requirements.

Distilled or Deionized water grade II shall be used for the preparation of all reagents and calibration standards and as dilution water.

**24.2.2 Nitric acid concentrated** (CAS No. 7697-37-2),  $\text{HNO}_3$  70 % w/w, analytical grade (redistilled), density 1.42 kg/L.

Use analytical grade with an arsenic content not greater than 10  $\mu\text{g/L}$  As.

**WARNING** Concentrated nitric acid is a strong, potentially harmful acid. Use proper safety precautions when handling it.

**24.2.3 Nitric acid solution** (CAS No. 7697-37-2), 3.2 mol/L (3.2 N).

**24.2.4 Potassium iodide** (KI) (CAS No. 7681-11-0), 150 g/L solution. Dissolve 15 g of potassium iodide in 100 mL of deionized water grade II. Store in an amber bottle.

**24.2.5 Potassium thiocyanate** (KSCN) (CAS No. 333-20-0), 50 g/L solution. Dissolve 5 g of potassium thiocyanate in 100 mL of deionized water grade II.

**24.2.6 Sodium borohydride** ( $\text{NaBH}_4$ ) (CAS No. 16940-66-2), 8 mm (0.3 in.) pellets, weighing ~0.25 g each.

**24.2.7 Sodium hydroxide** (NaOH) (CAS No. 1310-73-2), ACS reagent grade.

**WARNING** Sodium hydroxide is a strong, potentially harmful alkali. Use proper safety precautions when handling it.

**24.2.8 Sodium borohydride**, solution. Dissolve 30 g NaBH<sub>4</sub> in a 1 % NaOH solution (10 g NaOH per liter) and dilute to 1 L in a volumetric flask with deionized water grade II.

**24.2.9 Arsenic (III) oxide—As stock solution** (As<sub>2</sub>O<sub>3</sub>) (CAS No. 1327–53–3), 1 mL solution ≡ 1 mg As, which is equivalent to 1 mg/mL or 1 g/L As).

Dissolve 1.320 g ±0.001 g of arsenic (III) oxide in 100 mL deionized water grade II containing 4 g NaOH and dilute to 1 L with deionized water grade II.

Commercial As stock solutions are available and recommended as an alternative to preparing the stock solution.

**24.2.10 Arsenic (III) oxide—As intermediate solution**, 1 mL solution ≡ 10 µg As, which is equal to 10 µg/mL or 10 mg/L As.

Pipette 1 mL of the arsenic stock solution (see 24.2.9) into a 100 mL volumetric flask and bring to volume with 3.2 mol/L HNO<sub>3</sub>.

**24.2.11 Arsenic (III) oxide—As working solution**, 1 mL solution ≡ 1 µg As, which is equivalent to 1 µg/mL As).

Pipette 10 mL intermediate arsenic solution (see 24.2.10) into a 100 mL volumetric flask and bring to volume with 3.2 mol/L HNO<sub>3</sub>.

#### 24.2.12 AA Spectrophotometer

Any commercial AA unit having an energy source, a heated quartz tube (preferred) or an atomizer burner system, a monochromator, a detector, and background compensation is suitable. The manufacturer's recommendations for instrument settings for As should be followed.

NOTE With the heated quartz tube hydride generation system, experimental results indicate that a background correction is not required.

#### 24.2.13 Arsenic hollow-cathode or electrodeless discharge lamp.

**24.2.14 Arsine generator** comprised of a reaction flask of ~125 mL capacity fitted with inlet-outlet tubes for argon flow through the solution and a device for adding sodium borohydride in a closed system.

NOTE Arsine generators are available commercially from instrument manufacturers and can have configurations slightly different from that described above.

#### 24.2.15 Acid digestion bomb, stainless steel shell, thick-walled PTFE cup and cover, typical volume 23 mL.

Such vessels, which are commercially available from several manufacturers, shall be leak proof and airtight when sealed, and shall be capable of withstanding operating temperatures of at least 110 °C (230 °F) and pressures of at least 1400 kPa (200 lbf/in.<sup>2</sup>). Typical capacities are in the range of 21 mL to 25 mL or higher, 45 mL.

**CAUTION** Check integrity of the cup before and after any usage. Pinhole through the lining may affect safety and may dissolve the metal body from the acid digestion bomb. Inspect the cup before any usage.

#### 24.2.16 Oven, regulated to 80 °C ±1 °C (176 °F ±2 °F).

**24.2.17 Filtration cell**, any apparatus capable of filtering the digested sample through filter paper (as per 24.2.18).

**24.2.18 Filter paper**, quantitative, ashless, medium filtration rate, grade 40 (see 5.3.13), or grade 42 (see 9.3.6) or equivalent, circle 110 mm.

#### 24.2.19 Analytical balance, with accuracy of 0.0001 g (0.1 mg).

## 24.3 Preparation of As Standards

### 24.3.1 As standard 0.025 µg/mL

Transfer 2.5 mL of the As working solution (24.2.11) to a 100 mL volumetric flask and bring to volume with 3.2 mol/L HNO<sub>3</sub>.

### 24.3.2 As standard 0.05 µg/mL

Use 5 mL of As working solution (see 24.2.11) and dilute as per 24.3.1.

### 24.3.3 As standard, 0.075 µg/mL

Use 7.5 mL of As working solution (see 24.2.11) and dilute as per 24.3.1.

### 24.3.4 As standard 0.10 µg/mL

Use 10 mL of As working solution (see 24.2.11) and dilute as per 24.3.1.

## 24.4 Sample Digestion

To prepare digested volume,  $V_0$ , of the barite sample, the following procedure shall be applied.

- a) Accurately weigh a 0.250 g representative barite sample to 0.0001 g (0.1 mg), record mass as  $m \pm 0.0001$  g ( $\pm 0.1$  mg) and place in the PTFE digestion cup.
- b) Add 10 mL concentrated HNO<sub>3</sub>. Cover the PTFE cup, and mount inside the steel shell. Tighten steel lid onto the bottom section.

**WARNING** Nitric acid is a strong acid. Use proper safety precautions when handling it, particularly when it is used in a digestion vessel.

- c) Heat for 1.5 h  $\pm 5$  min in the oven at 80 °C  $\pm 1$  °C (175 °F  $\pm 2$  °F).
- d) Cool for approximately 1 hr at ambient temperature.
- e) Reheat for 1.5 h  $\pm 5$  min at 80 °C  $\pm 1$  °C (175 °F  $\pm 2$  °F).
- f) Cool to ambient temperature.
- g) Remove the cover carefully and decant into a 50 mL beaker.
- h) Rinse the vessel and lid several times with deionized water grade II and add rinse to the beaker.
- i) Add deionized water grade II to the beaker to bring volume to ~40 mL.
- j) Filter through filter paper into a 50 mL volumetric flask. Wash the beaker with small portions of deionized water grade II into the filter. Bring flask to  $V_0$  volume, 50mL volume-mark with deionized water grade II.
- k) To obtain a procedural blank, repeat 24.4 Item a) through Item i) without a sample of barite.

## 24.5 Analysis of Standards and Samples

Analyze of standards and samples for cadmium and lead shall be as per the following procedure.

- a) Switch on the AA instrument and configure according to the manufacturer's directions.

- b) For each analysis, add 1 mL aliquots of the standard solutions (see 24.3) and blanks [see 24.4 Item k)] to the arsine generator. Add 2 mL of the potassium thiocyanate (KSCN) solution, 2 mL of the KI solution and 15 mL of 3.2 mol/L HNO<sub>3</sub>.

NOTE Aliquots larger than 1 mL can be required with some systems.

- c) Allow 10 min ±30 s for the As to be reduced to the trivalent state.
- d) Connect the generator and add one NaBH<sub>4</sub> pellet or pump NaBH<sub>4</sub> solution until the maximum signal is obtained according to the manufacturer's specifications. Record the peak height. When the recorder returns to the baseline, disconnect the generator.
- e) Prepare a standard curve by plotting peak height versus micrograms of As for each standard.
- f) Run sample solutions using 0.5 mL to 5 mL or more (from the total of 50 mL) in the same manner as for the standards [see Item b) through Item e)]. Record sample solution volumes as  $V_{s,g}$ .

NOTE To minimize As absorption losses on glassware, run the analysis on the standards and sample immediately upon preparation.

## 24.6 Calculation

**24.6.1** Using the sample absorbance from the calibration curves from 24.5 Item e), the As mass,  $m_{As}$ , expressed in micrograms, in the digested sample, subtracting any procedural blank (which is expected to be essentially zero) shall be determined.

**24.6.2** Mass concentration of arsenic in barite sample,  $c_{As}$ , expressed in milligrams per kilogram, shall be given in Equation (41).

$$c_{As} = \frac{m_{As}}{V_{s,g}} \times \frac{V_o}{m} = m_{As} \times \left( \frac{V_o}{m V_{s,g}} \right) \quad (41)$$

where

- $m_{As}$  is the mass of arsenic in the digested sample, expressed in micrograms;
- $V_o$  is the volume of digested solution, expressed in milliliters (50 mL in this procedure);
- $m$  is the barite sample mass, expressed in grams;
- $V_{s,g}$  is the sample volume added to the generator, expressed in milliliters.

NOTE One milligram per kilogram is equivalent to one microgram per gram.

# Annex A (informative)

## Rational Analysis

### A.1 Principle

The chemical analysis results obtained from wet chemical analyses and X-ray fluorescence analysis of barite ores yield no details of the different mineral species that make up these ores. If limited assumptions are made, however, then the mineralogy or mineral composition may be deduced. This type of “logical” analyses to obtain the mineralogy of the barite ores is called rational analysis.

### A.2 Procedure and Calculation

**A.2.1** Assume all barium occurs as the sulfate, and all strontium as the sulfate. If wet chemical analysis is used, then these compounds are obtained directly.

If X-ray fluorescence is used to obtain the oxides, then barium sulfate mass fraction,  $w_{\text{BaSO}_4, \%}$ , and strontium sulfate mass fraction,  $w_{\text{SrSO}_4, \%}$ , expressed as percentages, should be given respectively in Equation (A.1) and Equation (A.2).

$$w_{\text{BaSO}_4, \%} = 1.522 \times w_{\text{BaO}, \%} \quad (\text{A.1})$$

$$w_{\text{SrSO}_4, \%} = 1.773 \times w_{\text{SrO}, \%} \quad (\text{A.2})$$

where

$w_{\text{BaO}, \%}$  is the barium oxide mass fraction by XRF analysis, expressed as a percentage;

$w_{\text{SrO}, \%}$  is the strontium oxide mass fraction by XRF analysis, expressed as a percentage.

**A.2.2** Acid soluble (HCl) iron is either siderite ( $\text{FeCO}_3$ ) or hematite ( $\text{Fe}_2\text{O}_3$ ). Pyrite ( $\text{FeS}_2$ ), being insoluble in HCL but soluble in  $\text{HNO}_3$ .

Pyrite mass fraction in barite sample,  $w_{\text{FeS}_2, \%}$ , expressed as a percentage, should be given in Equation (A.3)

$$w_{\text{FeS}_2, \%} = (2.148 \times w_{\text{Fe-nitric ac}}) - w_{\text{Fe-hydchlor ac}, \%} \quad (\text{A.3})$$

where

$w_{\text{Fe-nitric ac}}$  is the iron mass fraction by nitric acid digestion, expressed as a percentage (9.4);

$w_{\text{Fe-hydchlor ac}, \%}$  is the iron mass fraction soluble in HCl expressed as a percentage (Section 7).

**A.2.3** Hematite mass concentration may be obtained from the HCl soluble iron mass fraction. Hematite mass fraction,  $w_{\text{Fe}_2\text{O}_3, \%}$ , expressed as a percentage, should be given in Equation (A.4):

$$w_{\text{Fe}_2\text{O}_3, \%} = 0.699 \times \left[ w_{\text{Fe-hydchlor ac}, \%} - (0.482 \times w_{\text{FeCO}_3, \%}) \right] \quad (\text{A.4})$$

where

$w_{\text{Fe-hydchlor ac, \%}}$  is the iron mass fraction soluble in HCl, expressed as a percentage (Section 7);

$w_{\text{FeCO}_3, \%}$  is the siderite mass fraction, expressed as a percentage (Section 16).

**A.2.4** Aluminosilicate minerals include feldspars, clay, micas, and so forth. These may be approximated from alumina content.

Aluminosilicate minerals mass fraction,  $w_{\text{Al}_2\text{SiO}_5, \%}$ , expressed as a percentage, should be given in Equation (A.5).

$$w_{\text{Al}_2\text{SiO}_5, \%} = 2.7 \times w_{\text{Al}_2\text{O}_3, \%} \quad (\text{A.5})$$

where

$w_{\text{Al}_2\text{O}_3, \%}$  is the alumina mass fraction, expressed as a percentage (Section 7).

**A.2.5** Quartz (free silica) may be approximated by subtracting the silica in aluminosilicates from total silica concentration.

Quartz mass fraction,  $w_{\text{Quartz, \%}}$ , expressed as a percentage, should be given in Equation (A.6).

$$w_{\text{Quartz, \%}} = w_{\text{SiO}_2, \%} - (0.47 \times w_{\text{Al}_2\text{SiO}_5, \%}) \quad (\text{A.6})$$

where

$w_{\text{SiO}_2, \%}$  is the silica mass fraction, expressed as a percentage (Section 6);

$w_{\text{Al}_2\text{SiO}_5, \%}$  is the mass fraction of aluminosilicate minerals, expressed as a percentage (A.2.4).

**A.2.6** Calcium sulfate (e.g. gypsum) should be obtained from the water-soluble calcium as given in Equation (A.7). This is assuming that there is no calcium chloride ( $\text{CaCl}_2$ ) present.

Gypsum mass fraction,  $w_{\text{Gypsum, \%}}$ , expressed as a percentage, is given in Equation (A.7).

$$w_{\text{Gypsum, \%}} = 4.295 \times w_{\text{Ca-aq, \%}} \quad (\text{A.7})$$

where

$w_{\text{Ca-aq, \%}}$  is the calcium mass fraction of water-soluble minerals, expressed as a percentage (Section 10).

**A.2.7** Calcium carbonate mass fraction,  $w_{\text{CaCO}_3, \%}$ , expressed as a percentage, may be approximated from the difference between the HCl-soluble Ca and the water-soluble Ca (assuming no lime or cement was detected) as given in Equation (A.8):

$$w_{\text{CaCO}_3, \%} = 2.479 \times (w_{\text{Ca-hydchlor ac, \%}} - w_{\text{Ca-aq, \%}}) \quad (\text{A.8})$$

where

$w_{\text{Ca-hydchlor ac, \%}}$  is the calcium mass concentration of HCl-soluble minerals, expressed as a percentage (Section 7);

$w_{\text{Ca-aq, \%}}$  is the calcium mass concentration of water-soluble minerals, expressed as a percentage (Section 10).

**A.2.8** *LOI* is due primarily to loss of  $\text{CO}_2$  by carbonates, and secondarily to loss of water from clays.

**A.2.9** The above “scheme” of rational analysis is strictly for purposes of an example. Other schemes may be used if each scheme is chemically correct. Also, it would be simple to write computer programs that could make the calculations from such rational analyses very easy and fast to perform.

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