

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 ₄	Barite, barites, barytes	4.50	2.5–3.5
Strontium sulfate	SrSO ₄	Celestite	3.97	3.5
Barium carbonate	BaCO ₃	Witherite	4.30	3.5
Barium silicate	BaSi ₂ O ₅	Sanbornite	3.74	5
Calcium carbonate	CaCO ₃	Calcite	2.72	3
Calcium magnesium carbonate	CaMg(CO ₃) ₂	Dolomite	2.87	3.5–4
Magnesium carbonate	MgCO ₃	Magnesite	3.0	4
Calcium sulfate	CaSO ₄ •2H ₂ O	Gypsum	2.3	2
Calcium fluoride	CaF ₂	Fluorite	3.0	4
Iron (ferric) oxide	Fe ₂ O ₃	Hematite	5.2	5.5
Iron oxyhydroxide	Fe ₂ O ₃ •nH ₂ O	Goethite	3.3–4.0	5–5.5
Iron (II, III) oxide	Fe ₃ O	Magnetite	5.16–5.17	5.5–6.5
Iron carbonate	FeCO ₃	Siderite	3.7–3.9	3.5–4
Iron sulfide	FeS ₂	Pyrite	5.0	6–6.5
Iron sulfide	Fe _{1-x} S (x=0 to 0.2)	Pyrrhotite	4.6	4
Iron/copper sulfide	CuFeS ₂	Chalcopyrite	4.2	4
Lead sulfide	PbS	Galena	7.5	2.5
Zinc sulfide	ZnS	Sphalerite	3.9	3.5–4
Ferrous titanate	FeTiO ₃	Ilmenite	4.7	5.5
Silicon dioxide	SiO ₂	Quartz, sand, chert	2.65	7
Aluminosilicates:				
Feldspar	(Na,K)AlSi ₃ O ₈	Albite, microcline	2.6	6
Mica	KAl ₂ (OH) ₂ AlSi ₃ O ₁₀	Muscovite	2.85	2.5
Clays	Al ₂ Si ₂ O ₅ (OH) ₄	Kaolinite	2.6	2
	(Al,Mg)(OH) ₂ Si ₄ O ₁₀ (Na,Ca) _x •4H ₂ 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, ¹ *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 ² (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 ²	American Chemical Society
EPA ³	U.S. Environmental Protection Agency
GGT	Garrett Gas Train
IC	ion chromatography
ICP ⁴	inductively coupled plasma (spectrometry)

¹ International Organization for Standardization, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland; www.iso.org.

² American Chemical Society, 1155 Sixteenth Street, N.W., Washington, DC 20036, USA; www.acs.org.

³ Environmental Protection Agency, 1200 Pennsylvania Avenue, N.W., Washington, DC 20460, USA; www.epa.gov.

⁴ 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 ⁵	National Institute of Standards and Technology
OSPAR ⁶	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
$C_{Cd-hydrchlor\ ac}$	cadmium mass concentration in acid
C_{CO_3}	digested sample (HCl), expressed in micrograms per milliliter
	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
$C_{Metal-hydrchlor\ ac}$	metal mass concentration of HCl-soluble minerals in barite sample, expressed in milligrams per kilogram
$C_{Metal-hydrfluor,\ oxo\ ac}$	metal mass concentration of (HF-H ₂ SO ₄ -HNO ₃ -HClO ₄)-soluble minerals in barite sample, expressed in milligrams per kilogram

⁵ National Institute of Standards and Technology, Gaithersburg, Maryland, USA; www.nist.gov.

⁶ OSPAR Commission, The Aspect, 12 Finsbury Square, London, EC2A 1AS, United Kingdom; 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 ₂ 100/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_t	volume of 0.01 mol/L (0.02N) H ₂ SO ₄ 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 ₂ SO ₄ 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
$w_{Elemnt-barite, \%}$	element mass fraction in barite sample (as received), expressed as a percentage
$w_{Elemnt-ash\ barite, \%}$	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 (BaSO_4)

Sodium carbonate (Na_2CO_3) fusion, then gravimetric analysis.

4.3.2 Strontium sulfate (SrSO_4)

Sodium carbonate (Na_2CO_3) fusion, then atomic absorption (AA) analysis or inductively coupled plasma (ICP).

4.3.3 Silica (SiO_2) and alumina (Al_2O_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/H₂SO₄/HNO₃ 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/H₂SO₄/HNO₃) 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/H₂SO₄/HNO₃ mixture; the difference in Ca, Mg, and Fe values obtained by these two extractions can give estimates of these compounds in barite: fluorite (CaF₂), talc (hydrous magnesium silicate), montmorillonite (Mg is usually present in lattice structure), and pyrite (FeS₂).

4.3.6 Alternative methods for iron (Fe)

Extraction with nitric (HNO₃) or with hydrochloric/nitric (HCl/HNO₃) 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 (FeCO₃)

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

4.3.9 Total carbonate (CO₃⁻²)

Determine by the Garrett Gas Train (GGT) method.

4.3.10 Sulfide (S⁻)

Determined by the GGT method; alternative procedure—treat with 1 mol/L HCl or 0.5 mol/L H₂SO₄, analyze H₂S 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 (BaSO₄) and strontium sulfate (SrSO₄) in barites by fusion with sodium carbonate (Na₂CO₃), 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 (Na_2CO_3) (CAS No. 497-19-8), anhydrous, ACS grade powder.

5.2.3 Sodium carbonate solution (0.2 % w/w), 1.0 g Na_2CO_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), NH_4OH , 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 μm (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 $^{\circ}\text{C} \pm 20^{\circ}\text{C}$ (1830 $^{\circ}\text{F} \pm 35^{\circ}\text{F}$).

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 ⁷ or equivalent, quantitative, ashless, medium filtration rate, circle 110 mm.

5.3.14 Filter paper, grade 541 ⁸ 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 μ 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 ± 0.1 g Na_2CO_3 . Mix thoroughly with stirring rod. Cover the mixture with an additional 2.0 g ± 0.1 g Na_2CO_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.

⁷ 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 μ m (at 98 % efficiency); ash content <0.007 % by weight; basis weight: 95 g/m² (0.019 lb/ft²); thickness: 0.210 mm (0.008 in.).

⁸ 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 μ m (at 98 % efficiency); ash content <0.006 % by weight; basis weight: 82 g/m² (0.017 lb/ft²); 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 % Na_2CO_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 NH_4OH dropwise until fumes of ammonia (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 NH_4OH 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 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 H_2SO_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 % H_2SO_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 BaSO_4 precipitate should be white.

- p) Remove from furnace, and cool to room temperature in desiccator. Reweigh the BaSO_4 precipitate and annealing cup on the analytical balance to the nearest 0.001 g. Record precipitate mass as m .

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 SrSO_4 shall be used to obtain barium sulfate correction factor k , used in Equation (4) from the correction curve in Figure 1.

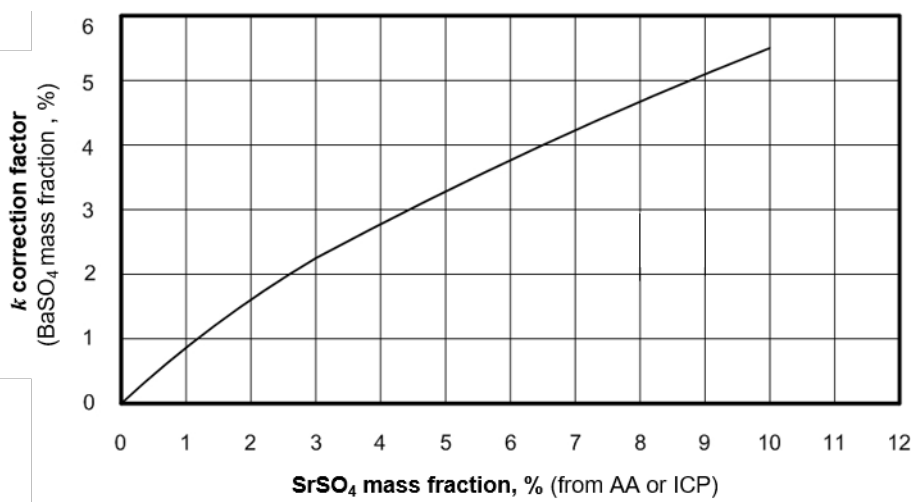


Figure 1—Typical Correction Curve for SrSO₄ in BaSO₄

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 (SiO₂) and alumina (Al₂O₃) 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 Al₂O₃ and SiO₂ 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 (NH₄)₆Mo₇O₂₄•4H₂O dissolved in 75 mL deionized water and 25 mL 20 % w/w H₂SO₄, 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 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 though 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 HSCH_2COOH 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 42⁹ 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 . 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 6mol/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

⁹ 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 μ m (at 98 % efficiency); ash content <0.007 % by weight; basis weight: 100 g/m² (0.020 lb/ft²); 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 SiO_2 and Al_2O_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).

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