

The Determination of Sulfate and Sulfide Sulfur in Rocks or Minerals

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CONTRIBUTIONS TO GEOCHEMISTRY

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THE DETERMINATION OF SULFATE AND SULFIDE SULFUR IN ROCKS OR MINERALS

By ANGELINA C. VLISIDIS

ABSTRACT

A method for the determination of sulfate and sulfide sulfur that occur together in rocks or minerals is presented. All the sulfate sulfur is converted to barium sulfate in an inert atmosphere to prevent oxidation of any sulfide sulfur. Cadmium chloride is added to precipitate any sulfide ion that may be liberated. The sulfate sulfur is then measured indirectly by the determination of the barium and is therefore unaffected by any subsequent oxidation of the sulfide sulfur. Total sulfur is determined on a separate sample, and sulfide sulfur is calculated by difference.

INTRODUCTION

A procedure is needed whereby insoluble sulfates and insoluble sulfides in a rock or mineral can be determined. A rock that contains sphalerite, pyrite, barite, and gypsum cannot readily be analyzed for sulfide and sulfate by any published method.

Approaches designed to isolate sulfide sulfur followed by the determination of the sulfate sulfur were tried and found wanting. For example, attack with tin and hydrochloric acid (Treadwell and Hall, 1919, p. 368-372) failed to dissolve insoluble sulfides in minerals such as chalcocite, bornite, and chalcopyrite. Tin and hydrobromic acid (Harding, 1881) or hydriodic and hydrochloric acids and mercury (Murthy and others, 1956, 1960), while effective in dissolving sulfide minerals, gave low results for sulfate sulfur, possibly because of partial reduction of sulfate ion.

Separation of the sulfate from the sulfide by selective solution of the sulfate in ammoniacal or sodium hydroxide solution of versene (Přibil and Maričová, 1952; Belcher and others, 1954; Morris, 1959) failed to dissolve barite completely. Prolonged boiling with a sodium carbonate-versene solution did dissolve the barite but also attacked some of the sulfide minerals.

In the method presented in this paper, sulfate sulfur is converted to barium sulfate by digesting the sample with an acidified solution of barium chloride in an inert atmosphere to prevent oxidation of any sulfide sulfur. Any insoluble sulfate present remains with the precipitated barium sulfate. Cadmium chloride is added to precipitate any sulfide ion that may be liberated in the digestion. This addition insures that no sulfide sulfur is oxidized in the initial filtration. The sulfate sulfur is then measured indirectly by the determination of barium in the barium sulfate precipitate and is, therefore, unaffected by any subsequent oxidation of the sulfide sulfur. Total sulfur is determined on a separate sample, and sulfide sulfur is calculated by difference.

PREPARATIONS

STANDARD SAMPLES

No analyzed standard samples containing both sulfate and sulfide were available for direct evaluation of this method. A sulfate standard was prepared of gypsum and barite (each ground to pass a 100-mesh sieve) mixed in the ratio 3:1. This was carefully analyzed for sulfate content.

Twelve of the more common sulfide minerals were also prepared as standards. After grinding to pass 100-mesh sieve each was treated with 1 percent hydrochloric acid at room temperature for 30 minutes, filtered, and washed with water to remove any sulfate that may have been present due to oxidation. Each sample was then dried with acetone, and placed in an airtight bottle. These samples were then analyzed for total sulfur, the values for which are given in the table as SO_3 .

REAGENTS

Cadmium chloride.....	10 percent w/v aqueous solution.
Barium chloride.....	10 percent w/v aqueous solution.
Hydrochloric acid.....	1 percent v/v aqueous solution.
Ammonium chloride.....	2 percent w/v aqueous solution.
Sodium carbonate.....	2 percent w/v aqueous solution.

PROCEDURE

Determination of sulfate sulfur

1. Transfer an accurately weighed 0.5000-gram sample to a 300-ml Erlenmeyer flask fitted with a two-hole stopper with a glass tube extending down into the flask.
2. Add 10 ml of CdCl_2 solution, 10 ml of BaCl_2 solution, and 200 ml of water and sweep out with nitrogen gas for 15 minutes.
3. Add 2 ml of conc HCl and heat the solution for one-half hour at about 50°C , continuing to bubble nitrogen through it. Remove from the heat, stopper, and let stand overnight.

4. Filter the solution through an 11-centimeter Whatman No. 42 paper; wash the residue 10 times with NH_4Cl solution to remove all the excess barium reagent (very important). Discard the filtrate.
5. Transfer the residue and paper to a platinum crucible and ignite. Cool.
6. Add 5 g of Na_2CO_3 and fuse.
7. Put the crucible into a 400-ml beaker, add about 200 ml of water, and digest on the steam bath until the cake is completely broken up.
8. Remove the crucible from the beaker, wash with water, dissolve any adherent material with 1+1 HCl and rewash. Add methyl-red indicator to the beaker and continue acidification of the solution with the HCl ; add an excess of acid so that all the salts except the insoluble sulfates go into solution.
9. Adjust the acidity of the solution to the proper concentration for the precipitation of BaSO_4 by first adding NH_4OH until the solution is just yellow—avoid an excess of ammonia—and then add 1+1 HCl drop by drop until the solution reverts to pink. Finally, add 3 ml of 1+1 HCl and dilute the solution to 300 ml.
10. Add 0.5 g of Na_2SO_4 , digest for 2 hours on the steam bath with occasional stirring, and let stand overnight.
11. Filter the solution, using a No. 42 paper, and wash the residue thoroughly 10 times with water to remove all the excess sulfate.
12. Transfer the residue and paper to a platinum crucible, burn off the paper, fuse with 5 g of Na_2CO_3 , and leach with water until the melt is completely broken up.
13. Filter, wash the precipitate and paper with Na_2CO_3 solution, and dilute to 300 ml. Add two drops of methyl-red indicator and 1+1 HCl dropwise until the solution becomes pink; then add 3 ml of 1+1 HCl in excess.
14. Add 10 ml of BaCl_2 solution slowly while stirring, digest the solution on the steam bath for 2 hours, and let stand overnight.
15. Filter on No. 42 paper and wash 10 times with water.
16. Burn off the paper in a weighed platinum crucible at a temperature below red heat. When all the carbon has been burned off, add one drop of 1+1 H_2SO_4 and a few milliliters of HF to the crucible. Evaporate the liquid on the steam bath, drive off the H_2SO_4 carefully, and ignite at 900°C in a muffle furnace for half an hour. Cool in a dessicator, weigh as BaSO_4 , and compute the SO_3 in the sample.

Determination of total sulfur

Determine total sulfur by any suitable method.

Calculation of sulfide sulfur

Subtract the value for sulfate sulfur from total sulfur to obtain the value for sulfide sulfur.

RESULTS

Table 1 lists the results of the analyses in which 0 to 0.1088 g of SO_3 from the sulfate standard was added to 0.2000-g samples of each of the 12 sulfide minerals.

TABLE 1.—Results of sulfide and sulfate sulfur analyses in which varying amounts of a sulfate standard were added to sulfide minerals

Sulfide mineral	Results of analyses in which were added indicated amounts of standard sulfate mixture, all amounts in grams of SO ₃				
	0.0000	0.0022	0.0218	0.0435	0.1088
Bornite (0.2000 g \approx 0.1271 g SO₃):					
Total sulfur.....	0.1271	0.1291	0.1482	0.1700	0.2355
Sulfate found.....	.0000	.0022	.0211	.0430	.1087
Sulfide calculated.....	.1271	.1269	.1271	.1270	.1268
Chalcocite (0.2000 g \approx 0.1051 g SO₃):					
Total sulfur.....	0.1051	0.1071	0.1268	0.1481	0.2136
Sulfate found.....	.0000	.0022	.0218	.0429	.1079
Sulfide calculated.....	.1051	.1049	.1050	.1052	.1057
Chalcopyrite (0.2000 g \approx 0.1673 g SO₃):					
Total sulfur.....	0.1673	0.1696	0.1893	0.2107	0.2758
Sulfate found.....	.0003	.0024	.0214	.0434	.1085
Sulfide calculated.....	.1670	.1672	.1679	.1673	.1673
Cobaltite (0.2000 g \approx 0.0883 g SO₃):					
Total sulfur.....	0.0883	0.0902	0.1099	0.1318	0.1967
Sulfate found.....	.0001	.0021	.0212	.0440	.1080
Sulfide calculated.....	.0882	.0881	.0887	.0883	.0887
Covellite (0.2000 g \approx 0.1587 g SO₃):					
Total sulfur.....	0.1587	0.1606	0.1803	0.2025	0.2677
Sulfate found.....	.0003	.0023	.0215	.0442	.1094
Sulfide calculated.....	.1584	.1583	.1588	.1583	.1583
Marcasite (0.2000 g \approx 0.2565 g SO₃):					
Total sulfur.....	0.2565	0.2584	0.2779	0.3010	0.3648
Sulfate found.....	.0001	.0024	.0213	.0438	.1081
Sulfide calculated.....	.2564	.2560	.2566	.2572	.2567
Pyrite (0.2000 g \approx 0.2615 g SO₃):					
Total sulfur.....	0.2615	0.2633	0.2827	0.3055	0.3694
Sulfate found.....	.0000	.0024	.0217	.0439	.1076
Sulfide calculated.....	.2615	.2609	.2610	.2616	.2618
Pyrrhotite (0.2000 g \approx 0.1842 g SO₃):					
Total sulfur.....	0.1842	0.1862	0.2050	0.2270	0.2921
Sulfate found.....	.0002	.0023	.0213	.0434	.1080
Sulfide calculated.....	.1840	.1839	.1837	.1836	.1841
Sphalerite (0.2000 g \approx 0.1632 g SO₃):					
Total sulfur.....	0.1632	0.1649	0.1860	0.2064	0.2713
Sulfate found.....	.0005	.0024	.0221	.0428	.1074
Sulfide calculated.....	.1627	.1625	.1639	.1636	.1639
Arsenopyrite (0.2000 g \approx 0.0140 g SO₃):					
Total sulfur.....	0.0140	0.0156	0.0351	0.0569	0.1231
Sulfate found.....	.0001	.0034	.0213	.0405	.1058
Sulfide calculated.....	.0139	.0122	.0138	.0164	.0173
Galena (0.2000 g \approx 0.0664 g SO₃):					
Total sulfur.....	0.0664	0.0693	0.0884	0.1103	0.1746
Sulfate found.....	.0002	.0027	.0210	.0466	.1072
Sulfide calculated.....	.0662	.0669	.0674	.0637	.0674
Stibnite (0.2000 g \approx 0.1318 g SO₃):					
Total sulfur.....	0.1318	0.1345	0.1540	0.1744	0.2411
Sulfate found.....	.0021	.0023	.0208	.0400	.1084
Sulfide calculated.....	.1297	.1322	.1332	.1344	.1327

Recoveries obtained were very satisfactory, although when arsenopyrite, galena, or stibnite was present the results were not as good as those obtained when any of the other nine sulfides were used. In samples where elemental sulfur is present, preliminary treatment with carbon disulfide to remove sulfur would be required. Any organically combined sulfur, of course, would be included in the total sulfur, and the sulfide sulfur would be in error. Sulfate-containing silicates, such as hauynite and noselite, and sulfide-containing silicates such as lazurite, helvite, and danalite are soluble in hydrochloric acid and present no problems.

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