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**SULFUR DETERMINATION
SUPPORTING
THE WASTE SOLIDIFICATION PROGRAM**

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and
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Chemistry

SULFUR DETERMINATION
SUPPORTING
THE WASTE SOLIDIFICATION PROGRAM

By

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SULFUR DETERMINATION SUPPORTING THE WASTE SOLIDIFICATION PROGRAM

INTRODUCTION

This paper presents an analytical method for the determination of sulfur in support of waste solidification studies. Waste solidification research requires accurate determination of the sulfur content of the feed material, the calcined powder, the fused solid, and the liquid condensates and scrubs. To calculate meaningful material balances for studying the behavior of sulfur during the solidification process, the analytical error must be no more than 5%.

The very purpose of waste solidification dictates that the products contain large amounts of diverse substances, especially compounds of fission product metals, and that the product be extremely insoluble. An analytical method that could be used for insoluble solids was required. Many of the published methods could be used only after dissolution of the sample and removal of interfering ions.

SUMMARY

Combustion with vanadium pentoxide proved to be an effective method of separating sulfur from a complex matrix such as the solid product from the solidification of fission product wastes.

After the sulfur has been volatilized from the sample in the form of sulfur trioxide, it is reduced to sulfur dioxide by hot copper turnings, removed from the off-gas stream, and quantitatively determined by titration or by colorimetry. Absorption in an iodine solution and back-titration of the excess iodine is used in the range of 1 to 5 mg of sulfur. The error is approximately $\pm 5\%$. A colorimetric determination employing pararosaniline hydrochloride and formaldehyde is used in the range 5 μg to 1 mg of sulfur with $\pm 10\%$ error.

This method, reported by J. G. Sen Gupta for sulfur determination in rocks,⁽¹⁾ is adaptable to the analysis of powders, solutions, and slurries. Oxides of nitrogen volatilized from the sample interfere with the determination but can be removed before combustion.

DISCUSSION

The classical gravimetric determination of sulfur as barium sulfate is beset with inherent inaccuracies. To obtain accurate results, removal of all anions and cations present in high concentrations is required. For materials containing appreciable amounts of sulfur in the presence of low concentrations of foreign substances, serious

interferences can be avoided by dilution; however, in waste materials of low sulfate content but with high concentrations of a wide variety of other salts, interferences are so serious that extensive clean-up is required before precipitation of barium sulfate.

Initially the gravimetric barium sulfate method was used for analysis of the various types of samples obtained during studies of waste solidification processes. Liquid condensates and caustic scrubs were analyzed directly with no sample pretreatment since they contained low concentrations of interfering cations. Solids and feed slurries were treated to remove the sulfur by acid leaching or by sodium carbonate fusion followed by leaching with water or hydrochloric acid. In nearly all instances, results were high (as much as 50%) because of failure to remove interferences. When Dowex-50 cation exchange resin was used to remove metallic cations, the accuracy of the analysis was considerably improved. However, complete removal of nitrate was necessary to obtain reliable results. After acid leaching or after treatment with ion exchange resin, repeated boiling to neat dryness with hydrochloric acid was effective in removing some of the nitrate interference, but was not satisfactory because the precision was poor, the procedure was time-consuming, and the results were generally high. When samples were fused with sodium carbonate, leaching with water was more satisfactory than leaching with hydrochloric acid.

Because of the difficulties encountered with the barium sulfate method, other methods found in the literature

were considered. For insoluble solids and for slurries, the combustion method reported by J. G. Sen Gupta was most promising. In this method sulfur is removed from the sample as sulfur trioxide by combustion with vanadium pentoxide, is reduced to sulfur dioxide with hot copper, and is determined iodimetrically or colorimetrically. The several advantages of this method are:

- Sulfur can be quantitatively recovered, even from such insoluble materials as barium sulfate.
- Sulfur is separated from all non-volatile sample components.
- Determination is fast and precise.
- The method requires less time than the gravimetric determination as barium sulfate.

This method was found to be adaptable to liquids, solids, and slurries. The range of the iodimetric titration is 1 to 5 mg sulfur; however, the upper limit can be extended by increasing the amount of iodine. The colorimetric determination which employs sodium tetrachloromercurate, formaldehyde, and pararosaniline hydrochloride, is much more sensitive and has a lower limit of approximately 5 μ g sulfur. Analytical error for the titrimetric determination is approximately $\pm 5\%$ while that of the colorimetric determination is about $\pm 10\%$.

Figure 1 shows the combustion apparatus that was used for both the titrimetric and the colorimetric procedures. The following conditions are critical to insure good recovery of the sulfur.

- The copper turnings must be kept bright and unoxidized. Daily re-

FIGURE 1. Combustion Assembly

placement with fresh copper may be required.

- A good grade of copper turnings is necessary. If cadmium is present in the copper, it will vaporize in the hot portion of the tube and condense as a metal mirror on the cooler surfaces. The hot cadmium will remove sulfur from the gas stream by the formation of cadmium sulfide, seriously reducing the yield of the analysis. If the quartz wool is not entirely in the hot zone of the furnace, the cadmium will condense on the surface of the quartz fibers; resulting in almost complete loss of sulfur.
- The combustion zone should be kept at 925 to 975 °C.
- The sample must be free of nitrate. Volatilization of oxides of nitrogen will inhibit development of color with pararosaniline or will cause release of iodine from the potassium iodide, producing low results. Nitrate may be removed by drying and baking the samples at 500 °C for half an hour before combustion.
- Solid samples must be finely ground and thoroughly mixed with the vanadium pentoxide. Infusorial earth, although it does not enter the reaction, improves the physical characteristics of the fused mass, permits better release of the sulfur trioxide, and extends the useful life of the combustion boats.

●Optimum combustion time is approximately 15 min; however, good results were obtained when the time was varied between 5 and 60 min.

The titrimetric procedure is designed for amounts of sulfur greater than 1 mg. This limit may be lowered by adjusting the concentration of the solutions involved in the titration; however, the starch-iodine endpoint is very poorly defined in dilute solutions, and the accuracy of the procedure deteriorates. For samples of low sulfur content the colorimetric method described by West and Gaeke⁽²⁾ can be used effectively.

For the colorimetric determination, the sulfur dioxide is scrubbed from the off-gas stream with sodium tetrachloromercurate and the color is developed with formaldehyde and pararosaniline hydrochloride. Absorbance is measured at 570 mμ. Rosaniline hydrochloride is a satisfactory substitute for pararosaniline hydrochloride.

The use of commercially available infusorial earth was found to result in high blanks unless the aliquot of the sodium tetrachloromercurate scrub solution used for color development was kept very small. When the sulfur content of the sample did not permit the use of a very small aliquot, good yields were obtained without the use of infusorial earth, but at the expense of a ruined boat.

RESULTS

Tables I and II illustrate the use of the titrimetric procedure in analyzing a synthetic feed solution.

Table III illustrates the variation in results obtained by analyzing

the same sample by several methods. (Actual sulfur composition is 4.85 g/liter.)

TABLE I. Composition of Synthetic Feed

Constituent	g/liter
Iron	14.03
H ₂ SO ₄ (a)	13.13
Cr(NO ₃) ₃ ·9H ₂ O	4.77
Ni(NO ₃) ₂ ·6H ₂ O	1.45
Al(NO ₃) ₃ ·9H ₂ O	515.84
Na ₃ PO ₄ ·12H ₂ O	229.00
H ₃ PO ₄	130.00
Na ₂ SiO ₃ ·9H ₂ O	1.43
ZrO(NO ₃) ₂ ·2H ₂ O	8.68
H ₂ MoO ₄	5.25
K ₂ CO ₃	1.45
La(NO ₃) ₃ ·6H ₂ O	25.72
CaSO ₄ (a)	2.3864
LiOH	28.76

(a) Total sulfur content is 4.85 g/liter.

TABLE II. Analyses of Synthetic Feed by Titrimetric Procedure

Sulfur found, g/liter		
4.94		
4.92	Average:	4.81
4.96	Range:	8.7%
4.64	Average Error:	2.8%
4.84		
4.94		
4.94		
4.76		
4.58		
4.54		

TABLE III. Comparison of Methods

Method	Sulfur Found, g/liter	
	Individual	Average
HCl digestion; gravimetric BaSO ₄	6.14	
	6.24	6.19
HCl digestion; Dowex-50 separation; HNO ₃ removal by evaporation with HCl; gravimetric BaSO ₄	5.74	
	5.61	5.68
Na ₂ CO ₃ fusion; H ₂ O leach; Dowex-50 separation; gravimetric BaSO ₄	4.14	
	4.80	
	4.73	
	4.63	4.58
Combustion with V ₂ O ₅ ; I ₂ titration	4.94	
	4.92	
	4.96	
	4.64	
	4.84	
	4.94	
	4.94	
	4.76	
Combustion with V ₂ O ₅ ; Colorimetric determination	4.58	
	4.54	4.81
	4.60	
	4.41	
	4.50	
	4.70	
	4.46	
	4.60	4.54

PROCEDUREEQUIPMENT

Two tube furnaces with quartz combustion tubes
 Nitrogen tank with pressure reduction valve
 Quartz combustion boats
 Buret and flask for titration
 Gas scrubber
 Timer or clock
 Spectrophotometer, Beckman Model B, 1-cm Pyrex cells

REAGENTS

Barium chloride, 10% solution
 Barium sulfate, reagent grade, dry
 Copper turnings, reagent grade
 Formaldehyde, 0.2% solution

Hydrochloric acid, 0.2N
 Hydrochloric acid, 12N
 Pararosaniline hydrochloride, 0.04% solution
 Potassium iodate, standard, 1.07 g/liter
 Quartz wool
 Sodium sulfate, standard, 1.000 g/liter sulfur
 Sodium sulfite, standard, 1.000 g/liter sulfur
 Sodium tetrachloromercurate, 0.2M
 Sodium thiosulfate, approximately 0.03M
 Starch-iodide solution; KI 45 g/liter, starch 4.5 g/liter
 Vanadium pentoxide, heated 4 hr at 900 °C, cooled, powdered, and

mixed with 0.3 times its weight of analytical grade infusorial earth

SAMPLE PREPARATION

SOLIDS

1. Crush to a fine powder.
2. Weigh and mix with approximately 1 g vanadium pentoxide-infusorial earth mixture directly in combustion boat.
3. If sample contains nitrate or nitrite, heat in oven for 30 min at 500 °C.

LIQUIDS AND SLURRIES

1. Place approximately 1 ml 12N HCl in 10 ml beaker.
2. Add carefully measured aliquot of sample.
3. Evaporate nearly to dryness.
4. Add approximately 10 drops 12N HCl and evaporate nearly to dryness.
5. Add approximately 1 ml BaCl₂ solution.
6. Dry carefully on hot plate until all moisture is removed.
7. Heat in oven at 500 °C for 30 min.
8. Remove from oven, cool, and mix thoroughly with microspatula, scraping all material loose from sides of beaker.
9. Add 1 g vanadium pentoxide-infusorial earth mixture.
10. Mix thoroughly and transfer to combustion boat.

COMBUSTION

1. Assemble combustion apparatus as in Figure 1.
2. Clamp all joints tightly to prevent leakage.
3. Adjust nitrogen flow to about four bubbles per second through

gas scrubber (Figure 2) containing small amount of water.

FIGURE 2. Gas Scrubber

4. Heat furnaces to specified temperatures.
5. Replace gas scrubber with appropriate scrubber and scrub solution for titrimetric procedure or colorimetric procedure.
6. Disconnect nitrogen supply at standard taper joint, insert combustion boat into combustion tube, and quickly reconnect nitrogen supply and adjust gas to about four bubbles per sec.
7. Set timer at 15 min.
8. After 15 min disconnect scrubber and remove combustion boat.

TITRIMETRIC DETERMINATION

Use the titrimetric determination for samples containing 1 to 5 mg sulfur.

Preparation of Standard Curve

1. Pour 65 ml 0.2M HCl into beaker or flask.
2. Add 10.0 ml KIO_3 solution.
3. Add 5 ml starch-iodide solution.
4. Add carefully measured aliquot of standard sulfite solution.
5. Titrate with thiosulfate solution to the disappearance of the blue color.
6. Plot milligrams of sulfur versus milliliters of thiosulfate.

Analysis of Sample or Solid BaSO_4 Standard

1. Place 35 ml 0.2N HCl in gas scrubber and 30 ml in test tube.
2. Add 10.0 ml KIO_3 solution to gas scrubber.
3. Add approximately 4 ml starch-iodide solution to gas scrubber and approximately 1 ml to test tube.
4. Follow sample preparation and combustion procedures outlined above.
5. Pour contents of scrubber and test tube into titration flask or beaker, using water wash to transfer quantitatively.
6. Titrate with thiosulfate solution to the disappearance of the blue color.
7. Determine recovery of sulfur in BaSO_4 using curve prepared with sodium sulfite standards.
8. Determine sulfur in samples from the curve, applying yield correction determined in Step 7.

COLORIMETRIC DETERMINATION

Use the colorimetric determination for sample containing 5 μg to 1 mg sulfur.

Preparation of Standard Curve

1. Make a fresh 1:20 dilution of the sulfite standard.
2. Pipet a series of aliquots of this dilute sulfite solution ranging from 0 to 200 λ (0 to 10 μg sulfur) into 1.0 ml tetrachloromercurate solution in a 10 ml volumetric flask.
3. Add 1.0 ml formaldehyde solution.
4. Add 1.0 ml pararosaniline hydrochloride solution.
5. Make to volume with water and mix thoroughly.
6. Allow to stand 30 min at room temperature.
7. Measure absorbance in 1 cm cells at 570 m μ using water reference.
8. Plot absorbance versus micrograms of sulfur.

Analysis of Sample or BaSO_4 Standard Solution

1. Pipet 10.0 ml tetrachloromercurate into a 1.5 by 20 cm test tube and insert outlet tube from combustion tube into this solution.
2. Follow sample preparation and combustion procedures outlined above.
3. After combustion is completed, remove aliquot of tetrachloromercurate scrub solution of appropriate size to give 0.5 to 4 μg sulfur and place it in 10 ml volumetric flask.
4. Add tetrachloromercurate solution to make a total of 1.0 ml.
5. Follow Steps 3 through 7 in the procedure for preparation of standard curve.

6. Determine micrograms of sulfur from standard curve.
7. Use analysis of BaSO_4 standard solution to determine yield.

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REFERENCES

1. J. G. Sen. Gupta. Analytical Chemistry, vol. 12, pp. 1971-1973, 1963.
2. P. W. West and G. C. Gaeke. Analytical Chemistry, vol. 28, p. 1816, 1956.
3. S. Barabas and J. Kaminski. Analytical Chemistry, vol. 35, pp. 1702-1705, 1963.