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DETERMINATION OF COMBINED SULFUR IN NUCLEAR REACTOR FUEL MATERIALS

by

L. E. Thorn, R. G. Bryan, and G. R. Waterbury

ABSTRACT

Combined sulfur is measured spectrophotometrically as the ethylene blue complex after separation from uranium and plutonium by hydrogen sulfide distillation. Higher sulfur oxidation states are reduced by a mixture of hydriodic acid, sodium phosphite, and acetic acid to hydrogen sulfide that is distilled into a zinc acetate solution. The acidic color reagent, NN-diethyl-p-phenylenediamine (DEPD), and ferric chloride react with zinc sulfide to form ethylene blue whose absorbance is measured at 675 nm after 15 min. Only those ions that interfere with the reduction or precipitate as highly insoluble sulfides cause interference in this method. The relative standard deviation is 10 to 1% for 2 to 30 µg of sulfate sulfur in samples containing up to 400 mg of uranium and plutonium.

I. INTRODUCTION

A spectrophotometric determination of sulfate (combined) sulfur in breeder reactor fuels, presented in LA-4622, pp. 95-99,¹ has been modified to improve its sensitivity and reliability. The first modification changed the reducing acid mixture from HI-H₃PO₂ to a mixture of HI, NaH₂PO₂, and CH₃COOH; the second substituted the complexing reagent DEPD for phenylenediamine. These changes also reduced the analysis time and eliminated adverse effects of uranium and plutonium. The major steps of the original method (1) sample dissolution, (2) reduction of sulfur to hydrogen sulfide and its distillation into a zinc acetate solution, and (3) formation of a colored complex and its spectrophotometric measurement, were not changed.

The sealed-tube method² is recommended for dissolving fuel materials in HCl to prepare solutions that can be analyzed without further treatment. The samples can be dissolved in HNO₃ and HF, but that solution must be evaporated to dryness on a steam bath and treated with formic acid to destroy nitrate ion before analysis. Nitric and formic

acids contain significant amounts of sulfur, so reagent blanks must be determined carefully.

Sulfate reduction to hydrogen sulfide is a highly irreversible reaction that few reagents are known to accomplish. The following half-reactions and potentials from Latimer³ indicate that the reduction is thermodynamically unfavorable:

High acid strength, high iodide to iodine ratio, rapid water removal, and high temperature favor the reaction, and rapid solution heating after addition of the reducing acids minimizes loss of sulfur, probably as sulfur dioxide. The reduction is carried out at the mixture's boiling point, and it is more than 90% complete in 10 min. The hypophosphite prevents formation of free iodine, and the acetic and hydrochloric acids keep the hydrogen ion concentration high.

A survey of existing color-forming reagents showed that DEPD is superior to its homologues, p-phenylenediamine and N-N-dimethyl-p-phenylenediamine, for determination of sulfide ion. Our work shows that DEPD reacts with ferric ion and sulfide within 15 min to form a complex that is stable for 16 h and whose absorbance is 2.5 times that of the p-phenylenediamine complex.

This method should determine sulfur as sulfate, sulfite, and probably sulfide, but not as free sulfur. The oxidizing atmosphere of either recommended dissolution method should convert sulfite to sulfate. If the sample is suspected of containing sulfide, bromine should be added to the acids used for dissolution.

II. PROCEDURE

A. Apparatus

Normal laboratory glassware, including beakers, volumetric flasks, pipets, and condensers.

Pressurized reducing-acid boiler, see Fig. 1.

Spectrophotometer, Beckman Model DU or equivalent, with matched 10-mm cell path length.

Sulfur distillation apparatus, see Fig. 2.

B. Reagents

Acetic acid, AR.

Argon gas. Nitrogen, CO_2 , or helium may be substituted as the carrier gas.

Distilled water, free from copper and other heavy-metal ions. Use for all dilutions.

Fig. 1. Pressurized reducing-acid boiler.

Fig. 2. Sulfur distillation apparatus.

Ferric chloride, 2% in 6N HCl. Dissolve 2 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 100 ml of 6N HCl.

Formic acid, reagent grade, redistilled.

Hydriodic acid, 57%, unstabilized. If this is not available, use 47% stabilized HI after distillation.

Hydrochloric acid, 12N, 6N, 3N, AR. Check for sulfur content by following the steps in Section III B, "Distillation and Color Development." Use only a reagent whose sulfur content is less than 0.5 $\mu\text{g}/10$ ml and prepare all dilutions using the same reagent and distilled water.

Hydrofluoric acid, 27N, AR.

Hydroxylamine hydrochloride, 20% aqueous solution.

N,N-diethyl-p-phenylenediamine (DEPD), also called p-aminodiethylaniline. Recrystallize from absolute alcohol, filter, and dry. Dissolve 1 g in 200 ml of 3N HCl to make a 0.5% solution.

Nitric acid, 15.6 N, AR.

Reducing Mixture. Mix 10 g of NaH_2PO_2 , 100 ml of acetic acid, and 400 ml of HI (57%) in the pressurized apparatus flask (Fig. 1). Boil the solution 30 min. Test for sulfur content by analyzing a 15-ml aliquot as described in Section III B, "Distillation and Color Development." If the sulfur content is above 0.5 $\mu\text{g}/15$ ml, reboil the solution in the pressurized apparatus.

Silver nitrate, 1% aqueous solution.

Sodium hypophosphite, AR.

Sulfur reference solution, 5 μg of sulfur/ml. Dissolve 2.7167 g of dry K_2SO_4 in water and dilute to 1 liter. Dilute 2.0 ml to 100 ml with 6N HCl.

Zinc acetate, 4% aqueous solution. Dissolve 20 g of $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ in 500 ml of water, let stand overnight, and filter.

III. SAMPLE ANALYSIS

A. Dissolution and Pretreatment of Sample

NOTE: Because the equipment is cold, the first analysis will give low results so it should be discarded.

1. If the sample was dissolved by the sealed-tube method, pipet an aliquot of the resulting solution containing from 2 to 30 μg of sulfur and up to 400 mg of sample into a 20-ml beaker and proceed to Section III B, "Distillation and Color Development."

2. If the sealed-tube method was not used, transfer a weighed portion of the sample containing from 2 to 30 μg of sulfur and weighing up to 400 mg to a 20-ml beaker or platinum dish.

3. Add 5 ml of H_2O , 5 ml of 15.6N HNO_3 , and 3 to 4 drops of 27N HF. Cover and heat the solution below its boiling point. If necessary, add more HNO_3 and HF. Also add the same amounts of acid to all blanks and reference solutions.

4. When the sample is dissolved, evaporate the solution just to dryness, but do not bake it.

5. Add 0.5 ml of formic acid dropwise, cover the beaker with a watch glass, and heat the solution moderately until the vigorous reaction subsides and gases are no longer evolved.

6. Remove the watch glass, rinse it with water, add the rinsings to the beaker, add 0.5 ml of formic acid, and slowly evaporate to near dryness.

7. Dissolve the residue in 1 to 2 ml of 3N HCl and proceed to Section III B, "Distillation and Color Development."

B. Distillation and Color Development

1. Add 1 ml of hydroxylamine hydrochloride and evaporate to near dryness.

2. Add 1 ml of H_2O to dissolve the residue and transfer it to a distillation flask (see Fig. 2) using 10 ml of 12N HCl. Add 15 ml of reducing mixture to the delivery bulb.

3. Insert the trap tube of the distillation apparatus into the trap.

4. Add 25 ml of H_2O and 10 ml of 4% $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution to a 50-ml, glass-stoppered, graduated cylinder and position the cylinder so

that the end of the delivery tube nearly touches its bottom.

5. Open the delivery bulb stopcock and insert the argon sweep tube. Tighten all connections and adjust the argon flow to 100 cm^3/min .

6. Turn on the heating mantle and boil the solution for 20 min.

7. Disconnect the distillate delivery tube and set it and the cylinder aside briefly while cleaning the apparatus and setting up the next distillation. Change the water in the trap.

8. Add 2 ml of DEPD solution through the distillation delivery tube to the cylinder containing the $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ solution. Wash the outside edges of the tube with water, stopper the tube, and mix the contents by inverting gently two or three times.

9. Immediately add 1 ml of 2% FeCl_3 solution, dilute to volume with water, and shake vigorously.

10. Let the solution stand at least 15 min, measure the absorbance at 675 nm against a reagent blank of water, $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$, 2 ml of DEPD, and 1 ml of 2% FeCl_3 solution.

11. Determine the micrograms of sulfur in the sample from a calibration curve prepared as described below, or calculate the sulfur using the calculated slope of the line and the equation

$$\text{Sulfur, ppm} = \frac{(\mu\text{g/abs of } S^-)(\text{abs of sample})}{\text{Sample wt, g}}$$

C. Preparation of Calibration Curve

1. Pipet four sets of aliquots containing approximately 0, 2, 5, 10, 20, and 30 μg of the sulfur reference solution and determine the sulfur by following steps 1 through 11 above. Subtract the average absorbance of the set without added sulfur from each of the other measured values, and plot the corrected absorbances as a function of micrograms of sulfur. Determine the slope and intercept of the line by a least squares calculation.

2. Redetermine two points, 0 and 10 μg of sulfur, on the calibration curve each time you analyze a series of samples. Two determinations at each of these two concentrations, one at the beginning and one at the end of the series of samples, are adequate to show proper functioning of the method.

3. If the blank reads more than 0.050 absorbance units, or the net absorbances do not agree with the calibration curve, prepare fresh reagents and redetermine the absorbances.

IV. EXPERIMENTAL

A. Reducing Acid Mixture

Gustafsson⁴ suggested that $\text{HI-NaH}_2\text{PO}_2\text{-HC}_2\text{H}_3\text{O}_2$ reducing acid gives less residual sulfur and fewer erratic results than $\text{HI-H}_3\text{PO}_2$. In our work, it had the added advantages of not precipitating the uranium and plutonium and of aiding in complete sulfur recovery from the matrix. We did not try to change the component ratio.

Optimum conditions for the reduction step were determined by varying the amounts of reducing acid mixture, HCl, water, and heat. With no uranium or plutonium present, 10 ml of reducing acid without HCl gave full sulfur recovery. When the actinide ions were present, sulfur recoveries were low unless 15 ml of reducing acid and at least 10 ml of HCl were used. We had to add water to the system when uranium and plutonium were present, because they were not soluble in the reducing mixture or HCl. The samples were dissolved in 1 to 2 ml of H_2O after evaporation on a steam bath and rinsed into the distillation flask with HCl. As much as 5 ml of H_2O could be tolerated.

All blanks, reference solutions, and samples are prereduced with hydroxylamine hydrochloride to retain the reducing power of the acid mixture. Sulfur recovery in the presence of plutonium was low without this prior reduction.

Rapid sample heating is necessary to prevent low recovery, presumably owing to loss as SO_2 . A blank is run and discarded to heat the apparatus before sample analysis. Minimal time is allotted for cleaning the apparatus and starting successive determinations, to allow the heating mantle to remain warm. The heating mantle cannot be left on continuously because the HCl added in transferring samples produces fumes that cause the system to back up when sealed. To test the distillation time, the collecting cylinders were changed every 5 min during distillation. Analyses of each cylinder showed that most of the sulfide was distilled during the first 10 min of heating and that it was completely distilled within 20 min (Table I).

TABLE I

SULFUR RECOVERY DURING DISTILLATION

Sulfur Added (ug)	Sulfur Recovered (ug)					
	5 min	10 min	15 min	20 min	25 min	30 min
10	1.5	8.3	0.5	< 0.1	< 0.1	< 0.1
20	0.3	15.6	3.7	0.4	< 0.1	< 0.1

B. Color Development

According to Bernthsen,⁵ ferric ion with NN-dimethyl-p-phenylenediamine (DMPD) gives a red oxidation product that reacts with hydrogen sulfide in several ways. Among other products, sulfide green, leucomethylene blue, and methylene red are said to be formed. The first two transform easily into methylene blue, and very little methylene red is formed. Gustafsson⁶ showed that the absorption curve for commercial preparation of methylene blue was essentially the same as that for the color formed by ferric ion and DMPD, except that the latter had a stronger absorption at about 500 nm. This band is probably from methylene red formed during color development. The same type of reaction is assumed for formation of ethylene blue (EB). The solution first becomes red, then turns blue (see fig. 3).

We studied how reagent concentrations and other conditions affect color development by using solutions containing known amounts of Na_2S . The amount of DEPD, usually 0.02% of the total 50-ml volume, was varied from 0.01 to 0.04%. Absorbances were slightly lower at 0.01% and the time required for the red color to fade and the solution to stabilize was longer at 0.04%. The ferric ion solution strength, usually 0.04%, was varied from 0.02 to 0.08% with no noticeable change. When the acid strength, normally 12 meq of HCl, was below 6 meq, the color did not develop completely, and above 18

Fig. 3. Chemical formulas for the reagent and final product.

TABLE II
STABILITY OF ETHYLENE BLUE COMPLEX VS TIME

Time (h)	Absorbance of Reference Solution Containing			
	0 $\mu\text{g S}$	5 $\mu\text{g S}$	10 $\mu\text{g S}$	20 $\mu\text{g S}$
0.25	0.019	0.199	0.394	0.748
1.0	0.016	0.196	0.393	0.738
2.0	0.016	0.196	0.392	0.746
3.0	0.016	0.196	0.394	---
16.0	0.019	0.196	0.392	0.743

meq, color development was slower with resultant decreased absorbance.

The order of addition of reagents is important. No color develops if the ferric solution is added before the DEPD reagent. For best results, the flask is stoppered and inverted gently two or three times after addition of the DEPD reagent. Within 60 ± 30 s, the 2% FeCl_3 solution is added and the solution is quickly diluted to volume and shaken vigorously. The color stability as a function of time is shown in Table II.

We investigated the Beckman Sulfide Specific Ion Electrode No. 39610 as another means for measuring the sulfur. Using the reduction and distillation procedure shown above, we collected the H_2S in 5.0 ml of sulfide antioxidant buffer (SAOB) containing plastic beads to increase H_2S contact with the solution. The millivolt response of the sulfide selective electrode was linear in relation to the logarithm of sulfide concentration between 0.3 and 100 $\mu\text{g/ml}$. However, because the responses at the lower levels were not so reproducible as the EB color development and the SAOB solution was unstable, we did not use the electrode further.

V. RELIABILITY

Throughout the year, we analyzed more than 150 reference solution aliquots containing 10 μg of sulfur using the recommended procedure. The relative standard deviation of these measurements was 5.5%, ranging from 9.5% for 11 measurements of 2 μg of sulfur to 1.5% for 11 measurements of 20 μg of sulfur (Table III). These data agree with the Lambert-Beer law and show that the average molar absorptivity of the EB complex is 58 000.

TABLE III
DETERMINATION OF
MICROGRAM QUANTITIES OF SULFATE SULFUR

S Taken (μg)	No. of Detn	Corr Av Abs at 675 nm ^a	Rel Std Dev (%)
2	11	0.073	9.5
5	12	0.168	12.
8	20	0.299	4.0
10	154	0.370	5.5
20	11	0.722	1.5
30	4	1.11	1.0

^aBlank subtracted.

Because standard samples of sulfur-containing uranium, plutonium and uranium, or plutonium were unavailable, we estimated the method's reliability from recoveries of 2 to 20 μg of sulfur as sulfate reference solution aliquots added to 100 to 500 mg of the respective high-purity metal matrices dissolved in HCl. Table IV shows the recoveries.

TABLE IV
RECOVERY OF SULFATE SULFUR FROM METAL MATRICES

Matrix	No. of Detn	S Added (μg)	Av S Recovered (μg)	Av Recovery (%)
100 mg U	3	4	3.7	93
100 mg U	7	10	9.8	98
200 mg U	3	8	7.7	96
200 mg U	4	10	10.3	103
400 mg U	3	16	15.2	95
100 mg PuU	4	2	1.9	93
100 mg PuU	4	8	8.1	102
200 mg PuU	4	2	2.5	125
200 mg PuU	4	8	8.1	102
500 mg PuU	4	2	2.2	109
500 mg PuU	4	8	7.6	95
100 mg Pu	5	2	2.2	110
100 mg Pu	4	10	10	100
100 mg Pu	4	20	20.7	104
200 mg Pu	5	4	4	100
200 mg Pu	4	8	8.3	104
400 mg Pu	6	10	10.2	102

VI. INTERFERENCES

Gustafsson's studies⁶ showed few serious interferences. The reagent reaction is specific for H_2S , and only those ions that interfere with the reduction or cause precipitation of highly insoluble sulfide are of consequence. Of the latter ions, copper and mercury must be avoided both before and after reduction. No study of other possibly interfering ions was necessary because of the completeness of Gustafsson's work.

VII. CONCLUSIONS

The modifications to the method have increased its sensitivity and reliability. The 58 000 molar absorptivity of the EB complex is 2.5 times greater than that of the previously used p-phenylenediamine complex. Consequently, 2, rather than 5, μg of sulfur can be determined. The precision of the modified method is $\pm 0.6 \mu g$ for 5 μg of sulfur and about $\pm 0.3 \mu g$ for more than 5 μg . These precisions were computed from results obtained over a year's time using different lots of HI and other reagents prepared at different times. The unmodified method gave erratic results probably because of the pre-

cipitate that uranium and plutonium formed with the previously used reducing acid mixture.

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