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SUBJECT: Determination of Trace Amounts of Sulfur in
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DETERMINATION OF TRACE AMOUNTS OF SULFUR IN FLUORIDE SALTS

T. W. Gilbert and J. C. White

ABSTRACT

A method has been developed for the determination of total sulfur in fluoride salts using the methylene blue procedure. Reduction of sulfate to hydrogen sulfide is achieved through the use of a new reducing mixture consisting of stannous chloride dissolved in concentrated phosphoric acid. The new mixture is effective on microgram amounts of sulfate and offers a major advantage over the red phosphorous reducing mixtures in that larger samples may be taken for analysis. The procedure has been applied to fluoride salts containing from 1 to 500 ppm of sulfur. The coefficient of variation of the method is 10 per cent.

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Due to its great sensitivity, the methylene blue method has found wide application for the determination of trace amounts of sulfur.^{1,2} White and coworkers³ determined total sulfur in fluoride salts by this method after reduction of sulfate to hydrogen sulfide with a mixture of red phosphorus, hydriodic acid, and formic acid.² Since the fluoride salts were not soluble in this mixture, small samples of the order of 200 mg were taken for analysis. When the sample size was increased to get greater sensitivity, erratic results for sulfur were obtained. The lower limit of determination by this method was 10 ppm.

In order to determine sulfur in fluoride salts in the range of one to 10 ppm, other methods for reducing sulfate to hydrogen sulfide were investigated. A mixture of phosphoric acid and stannous chloride has been used for this purpose, and has been found to be an effective reductant⁴ and also a satisfactory solvent for most fluoride salts.

Since the phosphoric acid reducing mixture has only been applied to the determination of quantities of sulfate in the 5 to 20 mg range, experiments were carried out to determine its effectiveness on microgram amounts of sulfate.*

Apparatus

The digestion-distillation apparatus shown in Figure 1 consists of a 50-ml round-bottomed flask with a gas inlet tube, a connecting U-tube, and a detachable delivery tube. A 50-ml volumetric flask is used as the receiving vessel.

The water-cooled condenser in the apparatus of Johnson and Nishita² was omitted because the low volatility of the phosphoric acid made it unnecessary. In addition, since the fluoride salts do not contain nitrates, the gas washing column containing a solution of pyrogallol and sodium dihydrogen phosphate was omitted.

*Footnote. Since the completion of this work, a study of the determination of microgram amounts of sulfate with the phosphoric acid-stannous chloride reagent has been published.⁵ Although there were minor differences in apparatus and technique, the procedure was essentially the same as that in this work. A lower sensitivity was observed ($0.00145 \mu\text{g S/cm}^2$ as compared to $0.00123 \mu\text{g S/cm}^2$), but, since a filter photometer instead of a spectrophotometer was utilized to measure the methylene blue color, the difference is to be expected. The method was applied to the determination of sulfate in commercial ferric chloride and in clays.

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FIGURE 1. APPARATUS FOR THE DETERMINATION OF
SULFUR IN FLUORIDE SALTS

Heat was supplied to the flask by means of a heating mantle connected to a Variac variable transformer. An iron-constantan thermocouple was utilized to measure the temperature of the mantle.

A stream of argon was used to sweep the hydrogen sulfide from the phosphoric acid into the receiving flask. Any traces of sulfur which might be present in the argon were removed by passing it through a two per cent solution of potassium permanganate containing mercuric chloride. The gas stream was then passed through a silica gel drier before reaching the hot phosphoric acid.

A Beckman Model DU spectrophotometer and one-cm absorption cells were used in making the absorbance measurements.

Reagents

Reducing Solution. Dehydrate 85 per cent phosphoric acid by heating to 305 to 310° C. After the acid has cooled, add 20 g of stannous chloride dihydrate for each 100 g of the dehydrated acid. Heat the mixture under a stream of carbon dioxide until the temperature once again reaches 305 to 310° C and the evolution of hydrogen chloride has ceased.

Argon or Nitrogen Purification Solution. Add 5 to 10 g of mercuric chloride per 100 ml of two per cent potassium permanganate solution.

Zinc Acetate-Sodium Acetate Absorbing Solution. Dissolve 50 g of zinc acetate dihydrate and 12.5 g sodium acetate trihydrate in one liter of de-ionized water. Filter before using.

p-Aminodimethylaniline Solution. Dissolve one gram of p-aminodimethylaniline sulfate in 750 ml of water. Add 200 ml of concentrated sulfuric acid, cool and dilute to one liter with water.

Ferric Ammonium Sulfate Solution. To 25 g of ferric ammonium sulfate add five ml of concentrated sulfuric acid and 195 ml of deionized water. Filter if necessary.

Standard Sulfate Solutions. Dissolve 0.543 g of potassium sulfate in one liter of water. One ml contains 100 µg of sulfur. More dilute standard solutions are prepared by making suitable dilutions.

Procedure

Add approximately 20 ml of the reducing solution to the distillation flask. (Fill a graduate to 25 ml and pour out as much of the viscous liquid as is practical.) Add one gram of fluoride salt and 500 mg of B_2O_3 ; then stir the solids into the liquid. Add five ml of zinc acetate solution and 35 ml of deionized water to the receiving flask. Assemble the apparatus shown in Figure 1 and start the flow of argon; then set the Variac to 65 volts and commence heating. After 30 minutes the temperature shown by the thermocouple should be about $340^\circ C$. Maintain the temperature of the mantle between 340° and $370^\circ C$ for an additional 30 minutes. Disconnect the receiving flask and delivery tube, and, with the delivery tube in the flask, add five ml of p-aminodimethylaniline solution. Stopper, mix, and add one ml of the ferric ammonium sulfate solution. Dilute to volume with water, stopper and mix thoroughly. Measure the absorbance of the solution at 670 m μ against distilled water after 10 minutes but within 24 hours.

Precision

Aliquots of the standard sulfate solution were evaporated to dryness in the distilling flasks before the addition of 20 ml of reducing solution. The previously described procedure was carried out, after which the intensity of the methylene blue color was measured. Results that were obtained on 5, 10, and 20 μg amounts of sulfur are shown in Figure 2. The dashed line indicates the slope of the calibration curve that Johnson and Nishita² obtained using the red phosphorus reducing mixture. Assuming a linear relationship of absorbance vs concentration, the coefficient of variation of the 14 determinations is 10 per cent.

Since these data were obtained over a period of about two weeks, it was believed that a day-to-day variation might be responsible for the rather low precision. For this reason, four calibration points, two blanks, and the amount of sulfur in two samples of the F-ZrF₄-UF₄ were established in succession. The results are given in Figure 3. Although the agreement appears to be somewhat better than in Figure 2, on such limited data it cannot be concluded that any real improvement was made. Duplicate samples indicated the presence of 23 and 25 ppm of sulfur.

The quantity of sulfur present as sulfide in the fluoride salts was estimated by carrying out a third determination in which anhydrous phosphoric acid that contained no stannous chloride was used as the reaction medium. The result showed 13 ppm of sulfur indicating that 54 per cent of the sulfur is in the sulfide form.

FIGURE 2 CALIBRATION CURVE OBTAINED ON THE HYDROGEN SULFIDE DISTILLED FROM STANDARD AMOUNTS OF SULFATE

FIGURE 3. CALIBRATION POINTS AND RESULTS OBTAINED ON DUPLICATE SAMPLES OF A TYPICAL FLUORIDE SALT MIXTURE

Application of the Method to the Determination of Sulfur in Various Fluoride Salts

Sulfur was determined in a number of fluoride salts using the previously described method. Two determinations were carried out on each sample at different times and using different batches of stannous chloride-phosphoric acid reducing solution. The sample weight was one gram in each case. The results are shown in Table I.

Table I
Sulfur Content of Some Fluoride Salts

<u>Salt</u>	<u>Source</u>	<u>Sulfur, ppm</u>	
NiF ₂	Baker and Adamson Reagent	475	530
NaF	Baker and Adamson Reagent	<1	<1
KF	Baker and Adamson Reagent	110	140
NH ₄ F	Baker and Adamson Reagent	<1	<1
Na ₂ SiF ₆	Baker and Adamson Reagent	17	5
CrF ₃	E. H. Sargent	25	<1
LiF	Baker's Analyzed C. P.	24	35
CsF	A. D. MacKay	185	110
FeF ₃	Special Preparation	17	35
CeF ₃	Special Preparation	55	60
ZrF ₄	Special Preparation	11	<1

Notes on Technique

Difficulty was experienced with severe bumping of the phosphoric acid and sucking back of the zinc acetate solution toward the end of the distillation. This was found to be caused by the condensation of sufficient moisture in the U-tube to form drops of water large enough to fall back into the hot phosphoric acid. Minimization of the sources of moisture eliminated this difficulty. Boric anhydride instead of orthoboric acid was used to complex fluoride. A silica gel drying tube was placed between the scrubber that contained permanganate and the distillation flask to remove water vapor carried in by the argon stream.

During the distillation of zirconium fluoride samples an unidentified white solid condensed in the U-tube. A small amount was carried over into the receiving flask causing a slight turbidity which disappeared on long standing. On two samples the turbidity was completely gone after 48 hours. The decrease in the absorbance of the solution over this period was observed to be about three per cent. Standard sulfate samples faded approximately 1.6 per cent in the same length of time. The error of one per cent introduced by the turbidity is therefore negligible when compared to the precision of the method. The solid deposit on the U-tube was washed out after each determination.

The importance of stirring the sample thoroughly into the phosphoric acid mixture must be emphasized. If this is not done, the sample tends to form a lump in the bottom of the flask which will not react completely even on long heating. It has been found experimentally that the results obtained on samples not well-stirred into the phosphoric acid can be as much as 47 per cent lower than results obtained on duplicate well-mixed samples.

Discussion

The phosphoric acid-stannous chloride reducing solution has two important advantages over the red phosphorus-hydriodic acid mixture employed by Johnson and Nishita. The latter mixture is known to give erratic results when the sample size and the volume of reducing mixture are increased beyond about 200 mg and 5 ml, respectively. With the phosphoric acid mixture, however, samples of one gram can be satisfactorily handled, thereby enabling lower percentages of sulfur to be determined. Secondly, the fluoride salt is not dissolved by the red phosphorus mixture, and thus some question arises as to whether all of the sulfur in the sample is exposed to the action of the reducing solution. Under the conditions used with the phosphoric acid mixture, however, uranium tetrafluoride, for example, is brought completely into solution and even zirconium tetrafluoride can be handled since it is converted to a white precipitate which is undoubtedly zirconium phosphate.

Figure 2 shows that the slope of the calibration curve obtained by Johnson and Nishita is substantially greater than that obtained using the phosphoric acid reducing solution. A number of factors could be responsible for this difference: (1) Incomplete reduction of the sulfate to hydrogen sulfide, (2) differences in the final acidity of the methylene blue solution or in the concentration or purity of the reagents employed, (3) incomplete absorption of the hydrogen sulfide in the zinc acetate solution, (4) incomplete removal of the hydrogen sulfide from the phosphoric acid solution, (5) greater losses of hydrogen sulfide on acidification of the zinc acetate solution with the solution of p-aminodimethylaniline.

No thorough investigation of the cause of this difference has been made, but the first two factors appear to be the more likely explanations. The third factor was studied in a single experiment with two absorption flasks connected in series. No hydrogen sulfide was found in the second flask. The last two reasons appear rather unlikely.

In connection with the possibility of incomplete reduction to hydrogen sulfide, mention should be made of the results of Kiba et al.⁴ who determined sulfur in a large number of metallic sulfates with the phosphoric acid-stannous chloride mixture. Good results were obtained on all the salts with the exception of copper sulfate where the results were about 50 per cent low. No explanation of this behavior was offered. Madsen and Madsen,⁶ however, were able to determine the sulfur in copper sulfate using an aqueous phosphoric acid-stannous chloride mixture by collecting and

titrating the SO_2 evolved. The possibility of the loss of SO_2 before complete reduction has been achieved must therefore be kept in mind.

The acid concentration and the concentration of zinc in the final solution have been reported to affect the intensity of the methylene blue color.² Since the reagent solutions were not accurately standardized, differences in the concentrations of reactants may have been sufficient to cause the difference in the slopes of the calibration curves.

A problem of a practical nature is that of the etching of the glassware by the acid fluoride solution. Although boric anhydride is added to the reaction mixture to complex the fluoride, etching is not completely eliminated. It is, however, greatly reduced. In view of the simplicity of the apparatus used, this difficulty is not of serious economic consequence.

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