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NEPHELOMETRIC DETERMINATION OF MICROGRAM QUANTITIES OF SULFATE WITH 2-AMINOPERIMIDINE

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NEPHELOMETRIC DETERMINATION OF MICROGRAM QUANTITIES OF SULFATE WITH 2-AMINOPERIMIDINE

by

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ABSTRACT

Sulfate was determined nephelometrically with 2-aminoperimidine sulfate suspensions at pH 2. The method was applicable from 2 to 30 μg of sulfate in 20 ml of sample, with an estimated relative precision of 10%. Procedures for purification and recovery of the 2-aminoperimidine hydrochloride reagent are given. After colored organic material was removed by a column of the polymeric adsorbent *Amberlite** XAD-2, the sulfate content of surface waters was determined with this method.

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* Trademark Rohm and Haas Company, Philadelphia, PA.

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NEPHELOMETRIC DETERMINATION OF MICROGRAM QUANTITIES OF SULFATE WITH 2-AMINOPERIMIDINE

INTRODUCTION

A continuing need exists for a simple reliable method of determining low-level sulfate concentrations in aqueous systems. Most classical methods are based on precipitation of sulfate as the sparingly soluble barium sulfate. Sulfate is then determined directly from the turbidity of barium sulfate suspensions or indirectly through determination of the bound or excess barium ion associated with the barium sulfate precipitation. These methods are limited in usefulness by the nature of the barium sulfate precipitate. Stable, reproducible suspensions are difficult to obtain; and the barium sulfate precipitate is seldom stoichiometric and without occluded ions.[1]

A new reagent for sulfate, 2-aminoperimidine (2AP), was described, and its use for a more sensitive nephelometric method was suggested.[2] Small uniform crystals of 2AP sulfate form a reproducible suspension suited to analytical measurement. This insoluble sulfate has been used, also, as the basis for sulfate determination by spectrophotometry[3] and pyrolysis.[4]

The nephelometric* method with 2AP offers more sensitivity than the barium sulfate turbidimetric* method with the same experimental simplicity. It was investigated particularly for application to analysis of surface waters at the Savannah River Plant (SRP). These waters are continually monitored for sulfate, but have a sulfate content sometimes below the limit of sensitivity of the conventional barium sulfate method. An analytical procedure for routine sulfate determination and procedures for purification and recovery of the reagent were established.

DISCUSSION OF METHODS

Barium Sulfate Method

The ASTM method for sulfate ion in water and waste water,[5] or its equivalent, is used at the Savannah River Laboratory for surface water analyses. Glycerin, ethanol, and sodium chloride

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* "Nephelometric" denotes measurement of intensity of light scattered at 90°; "turbidimetric," that of light transmitted.

are added to stabilize the barium sulfate suspension and to minimize interferences. The turbidity is determined with a spectrophotometer in a 5-cm cell at a wavelength of 450 nm. This method has the recognized disadvantages of difficultly reproducible suspensions and lack of sensitivity. Furthermore, many of the surface water samples are yellow. This color requires a large blank correction to the absorbance reading. Nevertheless, concentrations down to 1 ppm sulfate are reported.

2-Aminoperimidine Method

The method described by Stephen[2] consists of precipitation of the sulfate by adding a saturated solution of 2AP hydrochloride to the water sample at pH 5 to 7. The resulting suspension is measured nephelometrically. The precipitate of 2AP sulfate consists of particles about 2 μm in size, as shown by the scanning electron photomicrograph in Figure 1. In contrast to barium sulfate, the 2AP precipitate does not tend to agglomerate, and reproducible nephelometric readings are obtained over a period of several hours.

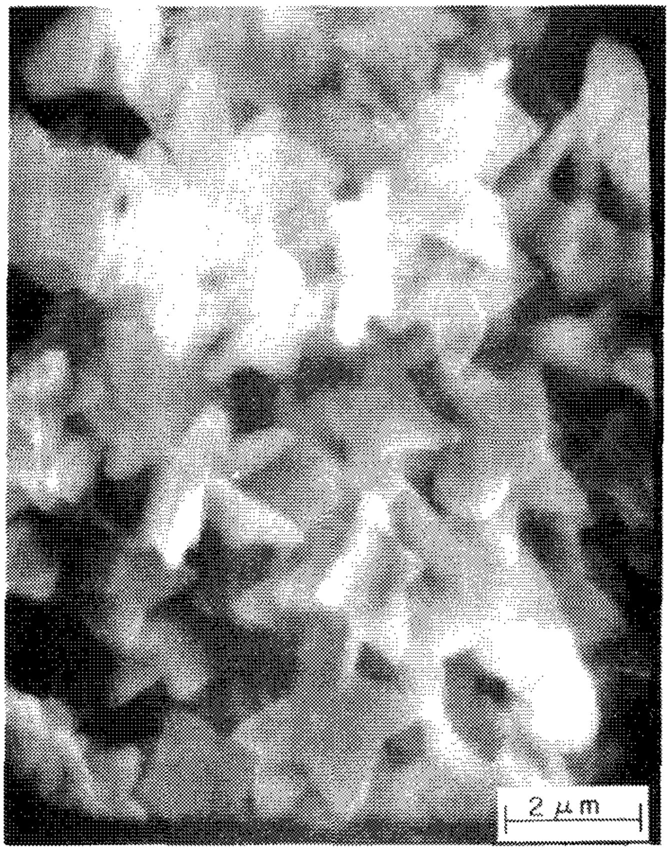

Figure 1. Scanning Electron Photomicrograph of 2-Aminoperimidine Sulfate

The analytical procedure[2] had to be modified before satisfactory results were achieved. Also, procurement, purification, and recovery of the 2AP hydrochloride differed from those that were described. Experience and general remarks are given below, and the stepwise procedures are given in Appendix A.

Most of the 2AP hydrochloride used was prepared on special order by PCR, Inc., according to the synthesis described by Stephen.[2] It was recrystallized once from methanol before use. A commercial source, G. Frederick Smith Chemical Company, provided a product which was used after it had been purified by two or three recrystallizations from methanol. Another synthesis has been published,[6] which appears to be superior, but it was not tried.

Because of the expense and scarcity of the reagent, all sample and reagent solutions were saved for recovery of the 2AP. The recommended procedure[2] for recovery consisted of converting the sulfate to the soluble hydroxide and then to the chloride. This approach was abandoned because of excessive degradation when the sulfate slurry was made alkaline. The simpler procedure of salting out the 2AP hydrochloride from the completed sample solutions by adding potassium chloride was adopted.

The reagent solution consists of a nearly saturated solution of 2AP hydrochloride in water. More-consistent results were obtained when a small amount of sodium sulfate was added to the freshly prepared solution, and the resulting 2AP sulfate precipitate was filtered out. Sometimes crystals formed in the solution on standing; these had to be redissolved or filtered out before the reagent gave quantitative results.

In the formation of the sulfate suspension, results were erratic with the neutral pH used by Stephen.[2] Above 20 μg sulfate, the nephelometer reading sometimes fell far below the expected linear response. Acidification of the sample solution to pH 2 reduced the sensitivity, but the readings were reproducible and linear with sulfate concentrations to >30 μg. Variation of the pH within a few tenths of a unit in the region of pH 2 did not affect the nephelometric measurements.

SRP surface waters often contained a substance that not only contributed a yellow color, but also inhibited precipitation of 2AP sulfate. The interferent was probably organic matter (humic or fulvic acids) from the vegetation the water had contacted. Pretreatment by acidification to pH 2 and passage through a column of *Amberlite** XAD-2 polymeric adsorbent[7] removed the color and the interference.

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TEST RESULTS

Figure 2 shows calibration curves. The ordinate is scaled in Nephelometric Turbidity Units (NTU), the unit of measurement of the instrument. The abscissa is expressed as micrograms of sulfate in the 25-ml total volume measured. Because as much as 20 ml of sample can be used, 10 μg of sulfate, for example, could correspond to as little as 0.5 ppm sulfate in the sample. In solutions acidified to pH 2, response was linear up to 40 μg. The insert in Figure 2 details the response below 5 μg. The two sets of calibration points were obtained with different batches of 2AP reagent; they illustrate the need to use the same batch of reagent for calibration and sample determinations. The blank was 0.1 to 0.5 NTU.

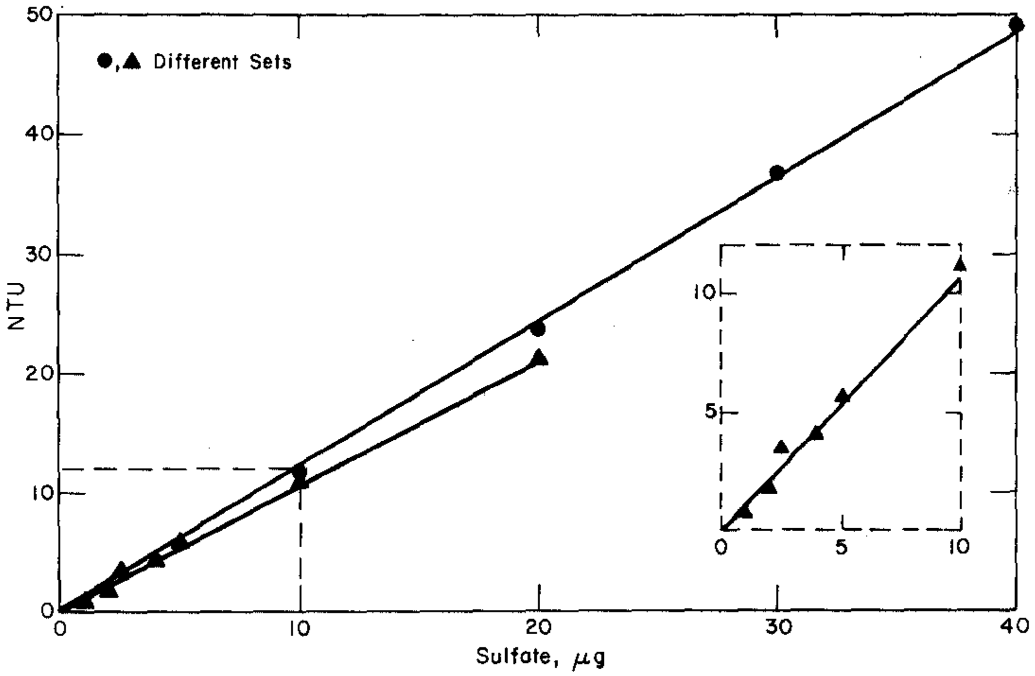

Figure 2. Calibration Curves for Nephelometric Determination of Sulfate with 2-Aminoperimidine

Table 1 compares the results of 10 µg spike recovery in surface water samples with 10 and 20 µg standards, all at pH 2. The acidified samples were pretreated by passing them through a column of *Amberlite* XAD-2. All are compared in terms of the slope of the linear response, as NTU/µg sulfate. The relative standard deviation for standards and spike recovery in the water samples was 3 to 4%. Although the slope for the recovered spike was 4% higher than for the standard alone, agreement is satisfactory. The precision for duplicate determinations would be ±10% at the 90% confidence limit; this is larger than the bias between the standards and spikes. The treatment with *Amberlite* XAD-2 did not affect recovery of sulfate. Variation of the volume of sample did not affect the sulfate concentration found.

TABLE 1

Nephelometric Measurements in Standards and in Surface Water Samples

Surface Waters					*Standards*	
Sample No.	*Volume, ml*	*NTU*	*Conc., µg/ml*[a]	*ΔNTU with 10 µg* $SO_4^=$ *added*	*NTU* *10 µg*	*20 µg*
1	3	11	3.5_2	11	10.5	19.5
	5	18	3.4_6	10	10	21
					9.5	20
2	5	6.7	1.2_9	10.8		20
	10	14	1.3_5		Mean = 1.00 NTU/µg $SO_4^=$ σ = 0.03	
3	5	6.5	1.2_5	10		
	10	13	1.2_5			
4	5	6.2	1.1_9	10.3		
	10	12	1.1_5			
5	5	6.8	1.3_1	10.2		
	10	15	1.4_4			
6	5	6.4	1.2_3	10.6		
	10	14	1.3_5			
7	3	11.5	3.6_9	11		
8	5	18	3.4_6	10		
				Mean = 1.04 NTU/µg $SO_4^=$ σ = 0.04		

---

[a] Calculated with 1.04 NTU/µg

In Table 2, results of single sulfate determinations made by the barium sulfate and 2AP methods are compared for a series of surface waters. The table shows the effectiveness of the *Amberlite* XAD-2 treatment in improving the barium sulfate turbidimetric determination through removal of the color and consequent reduction of the blank correction. Without the pretreatment, many of the $BaSO_4$ results were low compared to the 2AP. The low results and yellow color before pretreatment generally correlated. One rusty water sample had "too much color" for the $BaSO_4$ method. The *Amberlite* XAD-2 column filtered out the iron colloid, permitting "<1 ppm" to be reliably determined; this result agrees with the 0.2 ppm value obtained by the 2AP method.

TABLE 2

Comparison of Sulfate Determinations

Sulfate Concentration, µg/ml		
$BaSO_4$ Method		*2AP Method*
Without XAD-2 Pretreatment	*With XAD-2 Pretreatment*	*With XAD-2 Pretreatment*
9.0[a]	-	10
Too much color[a]	<1	0.2
<1[a]	1.0	1.2
1.1_5	1.6_9	1.5_8
1.1_0	1.5_4	1.4_7
1.0_8	2.0_1	1.7_0
0.8_7	1.5_4	1.5_1
0.9_7	1.6_9	1.6_0
1.5_6	1.6_4	1.6_1
1.9_0	1.6_0	1.5_4
1.7_1	1.7_7	1.6_6
1.4_1	1.6_1	1.6_4
1.4_9	1.6_7	1.6_7

Mean sulfate value (2AP) = 1.60 µg/ml

Mean relative bias ($BaSO_4$ - 2AP)

Without XAD-2 -17%

With XAD-2 +5%

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[a] Not included in calculations.

APPENDIX A

EXPERIMENTAL PROCEDURE FOR NEPHELOMETRIC DETERMINATION OF SULFATE WITH 2-AMINOPERIMIDINE

Apparatus

Hach Laboratory Turbidimeter, Model 2100A, or other nephelometer, with nephelometer tubes and turbidity standards (Hach Chemical Company, Ames, Iowa).

Millipore filter apparatus, such as Pyrex Microanalysis Frit Support, 25 mm, Cat. No. XX10 025 00 (Millipore Corporation, Bedford, Massachusetts).

MF-Millipore filter (0.45 micron pore size), Cat. No. HAWP 025 00.

Büchner funnel, or equivalent.

Filter paper, Whatman No. 41.

25-ml volumetric flasks.

Micropipet, such as *Digipet*, 1 ml (Manostat Corp., New York).

Assorted pipets as required.

Reagents

Standard Na_2SO_4 solutions, made from oven-dried Na_2SO_4.
Concentrated: 1000 μg sulfate/ml (1.479 g Na_2SO_4/liter).
Dilute: 100 μg sulfate/ml, made from concentrate.

Hydrochloric acid, 3M (1 volume concentrated HCl, 3 volumes H_2O).

Deionized water, acidified to pH 2 (4 ml 3M HCl per liter).

Potassium chloride (solid reagent and 0.1M KCl).

Methanol.

Diethyl ether.

2-Aminoperimidine hydrochloride, $C_{11}H_9N_3$ HCl, m.p. 282°C.[1]

- Purification of 2AP Hydrochloride by Recrystallization from Methanol

  1. Add about 1 g of 2AP hydrochloride to 20 ml of boiling methanol.
  2. Simmer, with stirring, until the 2AP dissolves; add a small amount more methanol if required to achieve dissolution.
  3. Filter hot liquid through filter paper, such as Whatman No. 41.
  4. Chill filtrate in ice about 1 hour.
  5. Filter on Büchner funnel (or equivalent).
  6. Wash crystals with cold methanol, then diethyl ether.
  7. Air dry the gray-to-tan crystalline product.

- Preparation of 2AP Reagent (0.5%)

  1. Add 0.125 g of 2AP hydrochloride to 25 ml of hot water.
  2. Stir to dissolve; cool to room temperature.
  3. Add 1 to 2 drops of 0.1M Na_2SO_4 to the cool solution.
  4. Stir for about 5 minutes.
  5. Filter through Millipore HAWP paper, 0.45 μ porosity.
  6. Store in dark glass bottle or away from light. Solution is stable several days.

  Note: If crystals appear on standing (the solution is virtually saturated), they should be removed before the reagent is used. These crystals can be removed by slightly warming or filtering the solution.

- Recovery of 2AP Hydrochloride from Sample Solutions

  1. After the sulfate determination, combine the solutions that contain 2AP.
  2. Add enough solid KCl to make the solution about 1M in KCl.
  3. Stir to dissolve. The solution will become turbid as the 2AP hydrochloride precipitates.

4. Allow to stand overnight.
5. Chill in ice; filter on Büchner funnel.
6. Wash with chilled 0.1M KCl, then diethyl ether. Air dry.

Procedure

Preparation of Standard Curve

1. From micropipet, place measured volumes of dilute sulfate standard corresponding to 1 to 30 μg of sulfate in 25-ml volumetric flasks.*
2. Dilute to about 20 ml with acidified water.
3. Add 4 ml of 2AP reagent from pipet, while swirling the solution; mix thoroughly.
4. Dilute to volume with water of pH 2; mix again.
5. After 5 minutes, determine turbidity of the suspension with nephelometer. The suspension is stable for several hours.
6. Make a graph of NTU versus μg sulfate, like Figure 1.
7. Save the solution after the determination for recovery of the 2AP.

Determination of Sulfate Content of Sample

1. Place volume of sample estimated to contain <30 μg sulfate in 25 ml volumetric flask.
2. Dilute to 20 ml, with acidified water if necessary; the solution should be at pH 2 at this point.
3. Proceed as with Steps 3, 4, 5, and 7 in "Preparation of Standard Curve."
4. Determine the μg sulfate in the sample from the standard curve and calculate the sulfate content in μg/ml with the volume of sample taken in Step 1.

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* The Hach Turbidimeter tubes used required 25 ml of solution.

APPENDIX B

EXPERIMENTAL PROCEDURE FOR PRETREATMENT OF SURFACE WATERS WITH "AMBERLITE" XAD-2

Apparatus

Ion exchange column, 8 mm OD with length to accommodate 20 cm column of resin.

Reagents

Amberlite XAD-2 (Rohm and Haas Co.)

Glass wool

Methanol

Procedure

Preparation and Maintenance of the *Amberlite* XAD-2 Column[7]

1. Wash the resin, as received from the manufacturer, by slurrying and decanting several times in water to remove the fines and the KCl mold retardant.

2. Transfer to ion exchange column enough resin to form a column about 20 cm long.

3. Wash column with 10 ml water at about 1 ml/min, but do not allow the level of the liquid to drop below the top of the resin at any time during the procedure.

4. Wash with about 10 ml methanol at about 1 ml/min.

5. Backflush the column with water to remove air bubbles that appear during the methanol wash.

6. Repack the column by allowing the resin to settle under water. Then wash the column with another 10 ml of water, downflow.

7. Place a plug of glass wool in the top of the column to hold the resin in place. (The glass wool also protects the column from contamination by particulates from unfiltered samples.) Replace the glass wool as required.

8. The column is now ready for use and can be used for sequential samples until the yellow color extends about 1/4 the length of the column. Then regenerate the column with about 20 ml of methanol and proceed from Step 5.

Pretreatment of Surface Waters

1. To 50 ml of sample, add 200 μl of 3M HCl.
2. Pour about 5 ml of the solution into the *Amberlite* XAD-2 column and pass it through at about 1 ml/min. Discard effluent.
3. Transfer remaining solution to column; pass through at about 1 ml/min. Use this effluent for sulfate determination.

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