A Simple Method of Sulfate Microdetermination

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Y. Yagi and one of the present writers (Egami)[1] devised a method to determine sulfate by dichromate titration method. Their method was modified by N. Tamiya[2]. Although the method has been shown to be sufficiently accurate and successfully applied to the microdetermination of sulfate in biochemistry, the procedure is rather complicated.

The present paper deals with the simplification of the method: sulfate is precipitated as barium sulfate, and the excess of barium is precipitated as barium chromate. Finally the excess of chromate is estimated in alkaline solution with a spectrophotometer at 375 mμ. The optical density and the quantity of sulfate are in the linear relation.

Analytical Procedure

(Reagents)

a) Barium chloride, 0.01M.

b) Potassium dichromate, a little more than 0.005 M.

c) Sodium acetate, 20% (w/v).

d) Sodium hydroxide, 1 N.

(Method of Analysis)

1) Six ml. or less of the neutralized test solution (containing sulfate sulfur in the range 10–300 γ) and 1 ml. of barium chloride are placed in a 10 ml. measuring flask, and the flask is allowed to stand for about one hour. The complete precipitation of barium sulfate takes place.

2) Two ml. of sodium acetate solution is added to the flask, and the flask is kept in an ice bath for twenty minutes.

3) One ml. of potassium dichromate is then added to the flask, the reagents are

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[1] Y. Yagi and F. Egami, *J. Chem. Soc. Japan.* **67**, 19 (1947).

[2] N. Tamiya, *J. Jap. Biochem. Soc.*, **22**, 59 (1950).

TABLE I

DETERMINATION OF SULFATE IN RAIN WATERS AND NATURAL SULFURIC ESTERS

Sample	Sample taken	Sulfur concn. found		Total sulfur when 60γ of sulfur was added to the sample* (γ)	Recovery (%)
		(γ)	(%)		
Potassium chondroitinsulfate	2.400mg	125	5.21	185	99.5
		126	5.25	187	
		130	5.42	186	
Potassium charoninsulfate	1.216mg	178	14.6	237	100.8
		183	15.0	251	
		186	15.3	244	
Rain water I	100ml	198	—	267	103.4
Rain water II	100ml	82	—	136	95.5

* A small quantity of sulfate added to the test solutions was always quantitatively recovered

TABLE II

DETERMINATION OF SULFATE IN SYNTHESIZED SULFURIC ESTERS

Sample	Sample taken (mg)	Sulfer concn.				Relative error (%)
		Calcd.		Found.		
		(γ)	(%)	(γ)	(%)	
Potassium ethyl sulfate	0.672	131	19.5	125	18.6	4.62
	1.058	206		202	19.1	2.05
Potassium p-nitrophenyl sulfate	0.985	123	12.5	130	13.1	5.37
	1.244	155		166	13.3	6.66

mixed well, the volume is brought to the 10 ml. mark with distilled water and the flask is kept cold for further twenty minutes.

4) The reaction mixture is transferred into a centrifugal tube. After being centrifuged, two ml. of the clear supernatant is mixed with 1 ml. of sodium hydroxide solution in a 10 ml. graduated test tube, and diluted to the volume with distilled water.

5) Then the extinction of this solution is measured at 375 mμ with the spectrophotometer**, and sulfate is estimated by the standard curve obtained by known sulfate solutions using the same reagent solutions.

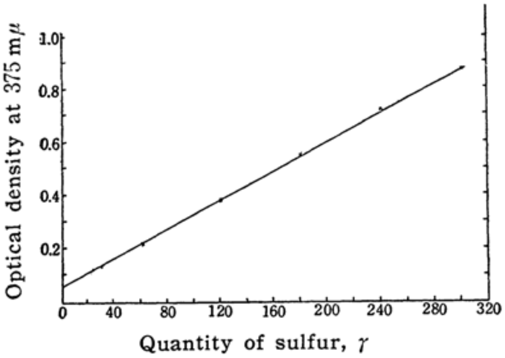

Fig. 1. A standard curve obtained by known sulfate solutions.

Remarks:

1) The optical density and the quantity of sulfate are in the linear relation as shown in Fig. 1. Each time, when barium chloride or potassium dichromate solution is renewed, the standard curve must be also renewed using known sulfate solutions.

2) When a convenient spectrophotometer is not available or the test solution has an absorption band near 375 mμ, sulfate might be estimated by a spectrophotometer at a different wave length in an alkaline or an acid medium. (c.f. the absorption spectra of chromate and dichromate. Fig. 2).

3) When a large quantity of phosphate coexists with sulfate, this method can not be applied as such, unless phosphate is removed before sulfate estimation[2].

Some Examples of Analysis

This method was successfully applied to the estimation of sulfate sulfur in some natural waters, and the natural and the synthesized sulfuric esters. (Table I and Table II).

For sulfuric esters, the analytical method was slightly modified. Each sample was hydrolyzed with 0.2 ml. of concentrated hydrochloric acid under the existence of 1 ml. of barium chloride, about 3 hours on a steam bath. The hydrochloric acid was removed by evaporation and the test solution was carefully neutralyzed.

For the rain water, one ml. of barium chloride solution was added to 100 ml. of the sample solution, and the solution was carefully concentrated to a suitable volume on a sand bath.

** We used Hitachi Type EPB-F spectrophotometer and cuvettes with a 1 cm light path.

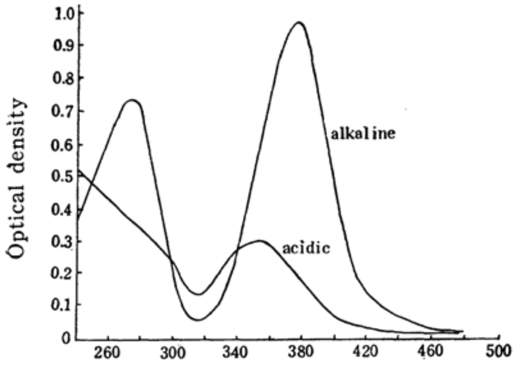

Fig. 2. The absorption spectra of chromate and dichromate (10^{-4} M).

Discussion

1) The extinction curve of the excess chromate revealed two strong absorption peaks at 273 mμ and 375 mμ in alkaline solution, and weaker one at 350 mμ in acid solution. (Fig. 2). The relationship between the amount of sulfate and the absorbance obeyed Beer's law over the range from 10γ to 320γ of sulfate sulfur. (Fig. 1).

2) Even the absorption at 375 mμ caused by the sample itself did not seriously interfere with the determination of sulfate. For example, although p-nitrophenyl sulfate (Table II) caused some absorption at 375 mμ after hydrolysis, analytical results showed it to be fairly good. In such a case, a blank without dichromate was necessary.

3) The good stability of the color of dichromate solution was also one of the advantages of this method.

Summary

1) A simple method for sulfate microdetermination was established. Sulfate is precipitated as barium sulfate; then the excess of barium is precipitated as barium chromate. Finally the excess of chromate is estimated in alkaline solution with a spectophotometer at 375 mμ.

2) This method is able to be applied to sulfate solution containing sulfate sulfur in the range 10–300γ. (30–900γ as SO_4^{2-})

3) This method was successfully applied to the estimation of inorganic sulfate such as that in rain water and organic sulfate such as chondroitinsulfate, charoninsulfate, ethyl sulfate and p-nitrophenyl sulfate.

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