

## Microdetermination of Sulphate by Indirect Spectrophotometry

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(Received 29th May, 1998, revised 1st April, 2000)

**Summary:** An indirect spectrophotometric method is developed for sulphate determination. The method is based on the reduction of sulphate to sulphide by fusing the sulphate sample with metallic sodium in solid state. The fused contents were dissolved in water and filtered. An aliquot of the filtrate was reacted with iron(III)-phenanthroline solution to reduce iron(III) to iron(II) which formed a red colour complex with 1,10-phenanthroline. Absorbance of the final solution was measured at 515 nm and plotted against sulphate concentration.

The method proved itself sufficiently accurate and precise and equally good for soluble and insoluble sulphates as well as for sulphate content in solid and liquid samples. The values of standard deviation and relative standard deviation calculated from absorbance values of ten solid samples of sodium sulphate were 0.006 and 0.82 % respectively. Effect of concerned parameters was checked and the developed method was applied for sulphate determination in a number of real samples

### Introduction

Sulphate is the most stable and abundant form of sulphur in which the element occurs in +VI oxidation state. Unfortunately no direct and simple spectrophotometric method could be so far developed for this important anion. Sulphate is either reduced to sulphide prior spectrophotometric determination or some indirect method is employed for its determination. Usually sulphate is reduced by a mixture of hydroiodic acid and hypophosphite to hydrogen sulphide, which is passed through zinc acetate solution and trapped as zinc sulphide. Then the sulphide suspension reacts with p-aminodimethylaniline and iron (III) to yield Methylene Blue[1]. P-Aminodiethylaniline is an alternative and more sensitive chromogenic reagent for sulphide determination [2]. Directly sulphate has been determined in water samples by forming complex with barium-dimethylsulphonazo-III complex [3,4]. The determination of small amounts of sulphate can be carried out turbidimetrically by adding a soluble barium salt to convert sulphate as insoluble barium sulphate[5].

Sulphate can be indirectly determined by treating the sample with barium chloranilate suspension. Sulphate ions form barium sulphate and displace an equivalent amount of chloranilate coloured ions [6]. 2-aminoperimidine has been proposed in different versions of indirect

spectrophotometric determination of sulphate [7]. Displacement of chromate[8] and iodate[9] from their chromium salts have also been employed for sulphate determination.

Sensitive indirect methods for sulphate determination are based on precipitation of sulphate ions with benzidine or 4-amino-4-chlorobiphenyl and then obtaining suitable azo-dyes[10, 11]. A number of other reagents like chlorophosphonazo-III [12], dimethylsulphorazo-III[13], sulphonazo-III[14], orthanilic-K[15] and nitro-orthanilic-S[16] have also been used for indirect determination of sulphate.

Most of the spectrophotometric methods for sulphide are based on its reducing properties. Hydrogen sulphide reduces molybdate in acidic media to molybdenum blue[17]. The redox reactions of sulphide with nitroprusside[18] and idonitrotetrazolium ion[19] have also been employed in the spectrophotometric determination of sulphide. Catalytic reduction of toluidine blue by sulphide has also been employed for its spectrophotometric determination [20].

Most of the methods mentioned above for the spectrophotometric determination of sulphate either need rarely available chemicals or involve strict

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control of conditions which make their use very limited. In present work, a relatively simple but sensitive method for sulphate determination is described. The method is based on the quantitative reduction of sulphate to sulphide by molten sodium. The resulted sulphide reduced iron (III) to iron (II) which reacted with 1,10-phenanthroline to give orange red complex. Absorbance of iron (II)-phenanthroline complex was measured at 515 nm. and plotted against sulphate concentration. Effect of a number of concerned parameters on the sulphate determination have been checked. To check the accuracy of the method, a number of real sulphate samples were analyzed by the described as well as a reference[6] method and the results were compared. .

## Results and Discussion

### Calibration and Precision:

Calibrations were prepared by using both the solid as well as liquid sulphate standards. In the case of solid standards, anhydrous sodium sulphate, in the range 2-10 mg were weighed and processed through the calibration procedure. To get the linear calibration, each sulphate standard after reduction with sodium, had to be diluted to 1000 times before reacting with iron (III)-phenanthroline reagent. Hence the final concentration of sulphate in the calibration solutions was in the range of 0.33-3.3  $\mu\text{g/mL}$ . However, in the case of liquid standards 0.01 - 0.05 mL aliquots of 10 mg/mL standard sulphate solution were used. A linear calibration

with the slope and intercept values 10.55 and 0.08875 respectively, obtained for the range 0.1 - 0.5  $\mu\text{g/mL}$  of sulphate is shown in Fig.1. The value of correlation co-efficient calculated for the calibration line was 0.9964.

Table 1 reveals the statistical data obtained from absorbance values of ten identical samples of solid sodium sulphate analyzed under same conditions.

Table-1. Statistical data analysis of ten solid sulphate samples

Sr.No.	Statistical data	Value
1.	Mean	0.244
2.	Median	0.244
3.	Mode	0.242
4.	Standard error	0.00063245
5.	Standard deviation	0.002
6.	Rel. standard deviation	0.82 %
7.	Sample variance	4E-06
8.	Conf. level (95.0 %)	0.001430715
9.	Skewness	0
10.	Range	0.006
11.	Minimum	0.241
12.	Maximum	0.247

### Effect of amount of sodium and Fusion Time

The quantity of sodium used for reducing sulphate sample was crucial in the sense that unused sodium in the fusion tube made the solution highly alkaline by forming sodium hydroxide. Hence to find out the adequate quantity of sodium metal, a number of equimolar sulphate samples were

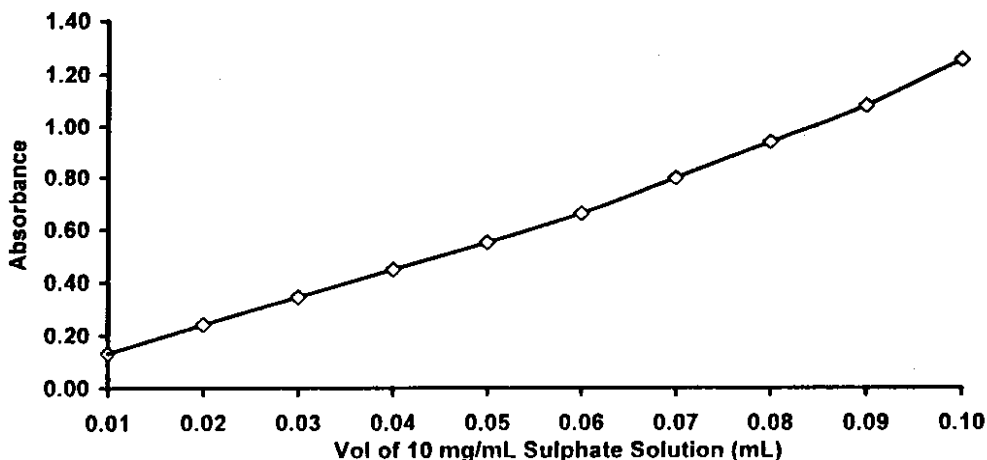


Fig. 1: Calibration of Liquid Standards of Sulphate

analyzed by reducing with different quantities of sodium ranging from 10 - 100 mg. As revealed by Fig.2, the optimum quantity of sodium necessary for reducing sulphate in the calibration range was 40-50 mg. By using lesser quantities of sodium, a significant decrease in the final absorption was found. However, greater quantities did not cause any considerable effect on the final absorption, rather a greater quantity of sulphuric acid had to be employed in that case to remove the turbidity caused by extra alkalinity.

Effect of fusion time was checked by fusing the equal quantity sulphate samples with the same amount of sodium metal for different time intervals ranging from 20 - 100 seconds. As shown in Fig.3, it was found that fusing time had a pronounced effect on the final absorption. The maximum absorption

was obtained when sulphate sample was heated with sodium metal for sixty seconds. Heating more than this time, caused a considerable decrease in the final absorption, which was probably due to the loss of sulphide by extra heating.

#### *Effect of Iron (III) to Phenanthroline Ratio:*

To check the effect of iron (III) and phenanthroline ratio a number of sulphate samples were analyzed by using different ratios of Iron (III) to phenanthroline. The ratio was changed by varying the volumes of molar solutions of iron (III) and phenanthroline. As shown in the Fig.4, a pronounced effect has been found by changing the ratio of the reagents. The optimum ratio of iron (III) to phenanthroline, at which the maximum absorption obtained, was found 1.4:1.6. Hence 3 mL of the mixture containing this ratio was used throughout the work.

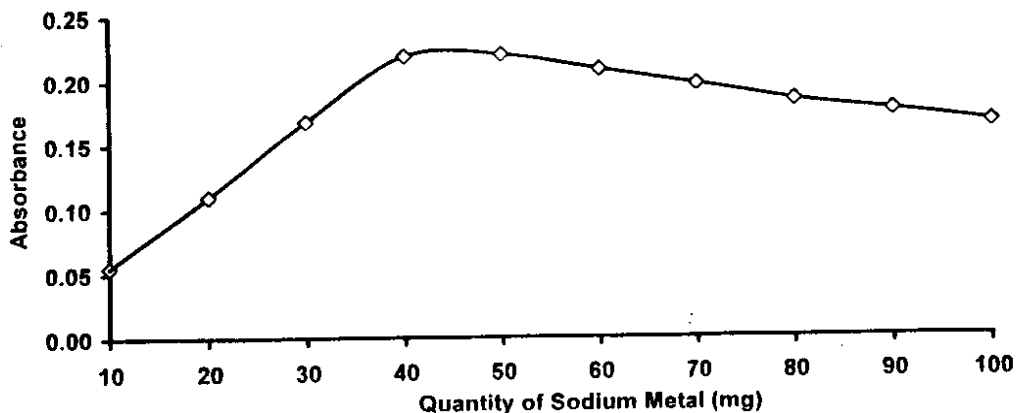


Fig. 2: Effect of Sodium Metal Quantity used for the reduction of sulphate samples

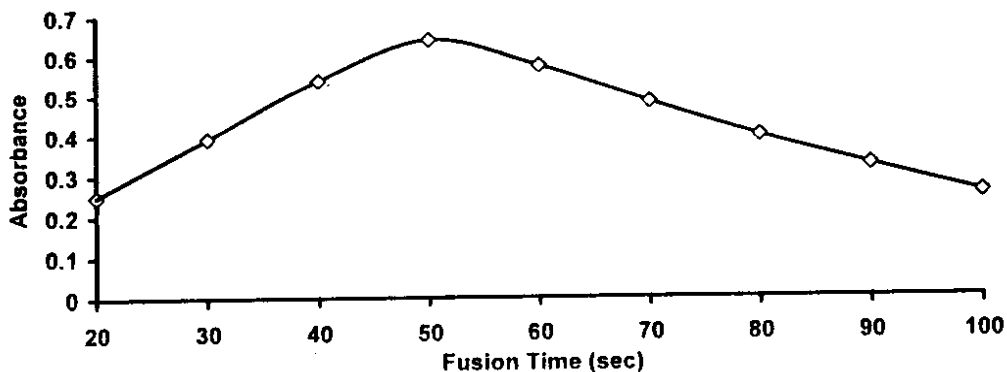


Fig. 3: Effect of fusion time

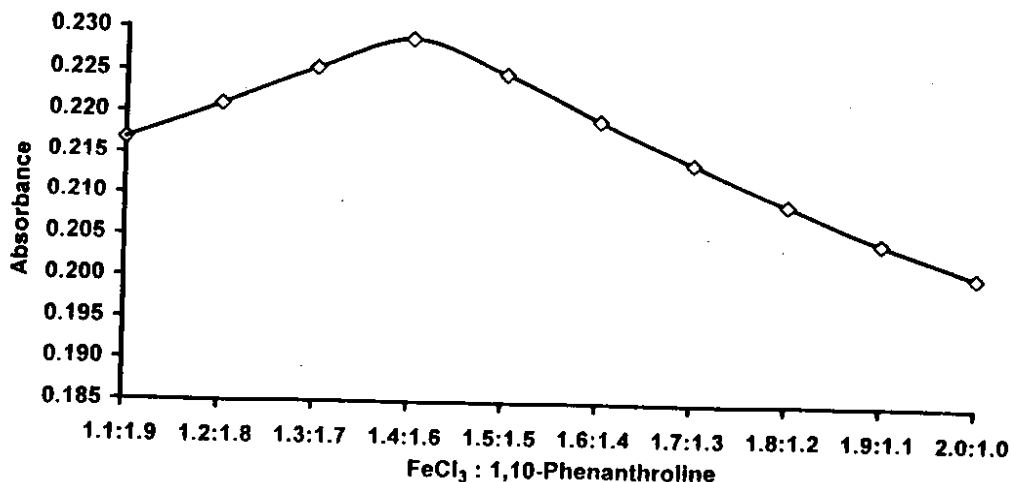


Fig. 4: Effect of ferric chloride - 1,10-Phenanthroline

*Effect of pH*

The pH could be critical in the described procedure of sulphate reduction, firstly because sulphide losses may occur in the form of hydrogen sulphide at lower pH values, secondly iron (III) may be precipitated as ferric hydroxide at higher pH, and thirdly iron (II)-phenanthroline complex formation could be pH dependent. Therefore the effect of pH was checked thoroughly by performing the sulphate determination at various pH values. Due to the presence of unused sodium metal the solution obtained after reduction of sulphate was highly alkaline and some times iron (III) was precipitated as hydroxide. To remove the turbidity therefore the pH of this solution was lowered by adding dilute sulphuric acid. When various samples, containing equal amounts of sulphate were analyzed, at different

pH values, the maximum absorbance of iron (II)-phenanthroline was found in the pH range 6 to 7. As shown in Fig.5, significantly lower absorption has been found at higher and lower pH values than this range

*Insoluble Sulphates and Conversion Percentage :*

The method was successfully employed for sparingly soluble sulphate salts. Standards of barium sulphate and lead sulphate were reduced in dry state with sodium metal and determined by the described procedure. Linear calibration was found for each salt when 2-10 mg of the salt was treated through the procedure. The linearity, slope and intercept found in the calibrations of barium and lead sulphates were almost same as obtained in the case of sodium sulphate.

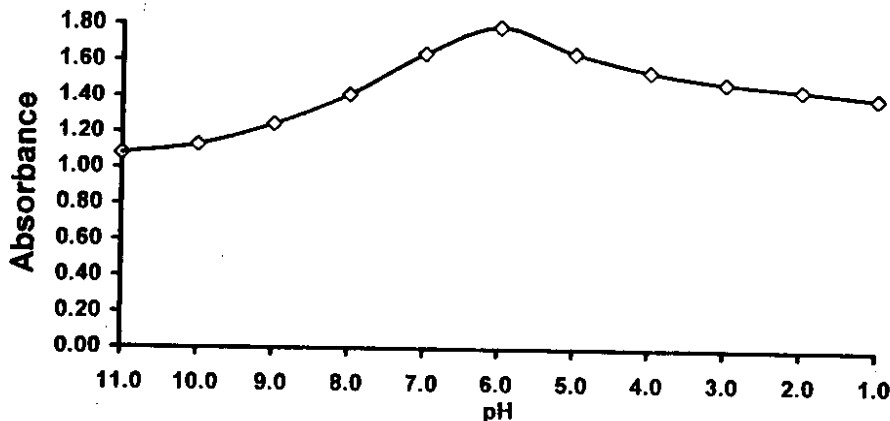


Fig. 5: Effect of pH

To check that how much sulphate actually converts into sulphide by reduction with sodium metal under described conditions, the average results of seven equal weight sulphate samples, treated through the given procedure, were compared with that obtained by using equivalent weight sulphide standard. As shown by the results in Table 2, first there is fairly acceptable precision in the results of sulphate samples and second in all the seven samples the conversion percentage was not less than 92%.

Table 2 : Percentage conversion of sulphate samples.

Serial No.	Absorption by sulphide converted from sulphate	Absorption by equivalent sulphide	Percent conversion.
1.	0.245		92.80
2.	0.246		93.18
3.	0.242		91.66
4.	0.246	0.264	93.18
5.	0.244		92.42
6.	0.243		92.04
7.	0.245		92.80
Mean	0.238	0.264	92.58

#### Effect of Interfering ions and Other Sulphur Species:

Effects of several possible interfering anions and cations have been checked on the described sulphate determination. The anions used were mostly of sodium and potassium while the cations were employed as their chloride and nitrate salts. The ions were added either in the same concentration as that of sulphate ions or in ten fold excess. As shown in Table 3, among the anions, only sulphite and thiosulphate interfered positively. The interference by these ions was expected because these species are also reduced into sulphide along with sulphate. Among the anions, only manganese depressed the final absorption to a considerable extent which could be attributed to its interference in iron (II)-phenanthroline formation.

Table 3 : Effect of interfering ions.

Interfering Anion	Added as	Absorption found	Interfering Cation.	Added as	Absorption found
Acetate (10x)	Sodium	0.244	Mercury	Nitrate	0.240
Nitrate (1x)	Potassium	0.242	Aluminum	Chloride	0.239
Phosphate (1x)	Sodium	0.238	Lead	Nitrate	0.235
Sulfite (1x)	Sodium	0.422	Calcium	Chloride	0.244
Thiosulphate(1x)	Sodium	0.391	Magnesium	Chloride	0.235
Chloride (10x)	Sodium	0.244	Manganese	Chloride	0.170
Carbonate (10x)	Sodium	0.241	Copper	Chloride	0.237
Bromide (1x)	Potassium	0.243	Nickel	Chloride	0.241
Nitrite (1x)	Sodium	0.241	Zinc	Nitrate	0.243

Absorption of 5µg sulphate taken as sodium sulphate = 0.245

An attempt was also made to check the effect of elemental sulphur on the determination of sulphate by the described procedure but every time when sodium sulphate and sulphur mixture was heated with sodium metal the fusion tube exploded violently.

#### Sulphate Samples:

To check the applicability of the proposed method, a few samples of sulphate containing fertilizer and coal ash have been analyzed by the described procedure as well as a reference method [6]. The results obtained by both the methods are shown in Table 4. The results of the most of the samples were in close agreement to each other. However the results of one sample of coal ash differ considerably with each other which may be attributed to in-homogeneity of the coal ash sample.

Table 4: Analysis of real sulphate samples

Sample	Sulphate found by proposed method µg/g	Sulphate found by reference method µg/g
Fertilizer Sample 1 (Amm.Sulphate Diluted)	325.5 (mean of 5 samples)	342.0 (mean of 5 samples)
Fertilizer sample 2 (Mixed Fertilizer)	286.5 (mean of 5 samples)	276.5 (mean of 5 samples)
Fertilizer sample 3 (Urea + Amm.Sulphate)	250.0 (mean of 5 samples)	262.5 (mean of 5 samples)
Coal Ash Sample A (collected from stack)	28.5 (mean of 3 samples)	30.5 (mean of 3 samples)
Coal Ash sample B (White residue)	16.0 (mean of 3 samples)	28.5 (mean of 3 samples)
Coal Ash sample C (Collected after burning of wood)	24.0 (mean of 3 samples)	22.5 (mean of 3 samples)

Fig. 1: Calibration of Liquid Standards of Sulphate

## Experimental

#### Chemicals, Apparatus and Equipment:

All the chemicals used, except sodium metal, were of AnalaR Grade. Laboratory made soft glass tubes with a small bulb at closed end were used for fusion of sulphate samples. Weighing at mg level was made on a five decimal single pan electric balance from A&D Electric Company, Japan.

Absorption measurements were made on a Pye Unicam SP8-400 UV/VIS Spectrophotometer in 10 mm glass cells.

#### Standard Solutions:

Iron (III)-phenanthroline reagent was prepared by mixing 2mL of 1M alcoholic solution of 1,10-phenanthroline and 1mL of 1M aqueous iron (III) chloride solution.

Sulphate standard solution 10 mg/mL was prepared by dissolving 1.48 g anhydrous sodium sulphate in 100 mL water.

#### Calibration Procedure

##### solid samples:

Solid samples of sodium sulphate in the range of 2-20 mg were directly weighed in fusion tubes. A small piece of sodium metal (approx. 50mg) was added to the sample and the tube was heated first gently and then strongly on a flame. The tube was heated until the completion of reaction, then the red hot tube was plunged into 5 mL cold water taken in a china dish. The tube and the burned material were crushed thoroughly and the contents were filtered and washed with 2 mL water. The filtrate and washings of each sample were collected in a set of 100 mL standard flasks.

A new set of solutions was prepared by diluting each of the above solution to ten times. One mL of each diluted solution was mixed with 3 mL of iron (III)-phenanthroline reagent in a set of five 100 mL standard flasks and one mL of 60 % sulphuric acid was added to the flasks to remove the turbidity of ferric hydroxide. The contents were left for ten minutes to complete the reaction. Then the volume of each flask was made up with water and absorbance was measured at 515 nm against a compensatory blank. The absorbance was plotted against sulphate concentration to obtain the calibration graph.

##### Liquid Samples

Aliquots in the range 0.01 - 0.05 mL, of 10 mg/mL standard sulphate solution were transferred into fusion tubes with the help of an Agla micro syringe. The tube was gently heated to evaporate the solvent. Then a piece of sodium ~ 50 mg was added and the contents were fused as described above. A set of final solutions was obtained in standard 10 mL flasks. One mL of the final solution was mixed with 3 mL iron (III)-phenanthroline reagent and one mL of 60% sulphuric acid. After ten minutes, each solution was diluted to the mark and absorbance of the complex was measured at 515 nm.

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