Determination of Sulphate by Gas-Phase Molecular Asborption Spectrometry

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Summary: A method has been developed to determine micro quantities of sulphate both in solid and liquid samples. The sulphate samples were reduced with a mixture of sodium hypophosphite, hydroiodic acid and acetic acid. The released hydrogen sulphide is swept to an optical cell and absorption measured at 203 nm, using a selenium hollow chathode lamp.

Introduction

Sulphate reduction to hydrogen sulphide offers an attractive basis for the estimation of this important ion. The hydrogen sulphate thus evolved can be determined spectrophotometrically as methylene [1,2] or ethylene blue [3]. Though this method is quite sensitive the colour development procedure is lengthy and tedious involving the use of a large number of reagents and very strict control of conditions. Moreover, the coloured complex is unstable [3] and hence to achieve reproducible results is difficult.

Gas-phase molecular absorption (GPMA) spectrometry has become important in recent years, and has been successfully applied for the determination of a number of ions [4,5]. Though the sensitivity of this method is slightly less than the spectrophotometric method the simplicity, speed, precision and accuracy make it more promising. Also the inteference experienced in methylene blu method [6] can be greatly reduced when gas-phase molecular absorption spectrometric method was applied.

Experimental

Apparatus and Reagents

Absoprtion measurement were made on Beckman Model 495 Atomic Absorption Spectrometer using a selenium hollow cathode lamp as a light source. A glass tube of 15 x 1.5 cm with quarts windows was used as an absorption cell. The apparatus used for reduction of sulphate was similar to that used by L. Gustafsson [2]. A schematic diagram of the system is shown in Fig. 1.

All reagents used were of AnalaR grade. Doublly distilled water was used throughout this work.

Reducing Mixture

Reducing mixture was prepared [7] by dissolving 5.0 g of sodium hypophosphite also called phosphinate (NaH_2PO_2) in 30 ml of glacial acetic acid and 70 ml of hydroiodic acid in a 200 ml round bottom flask. The mixture was refluxed for 30 minutes

*For correspondance.

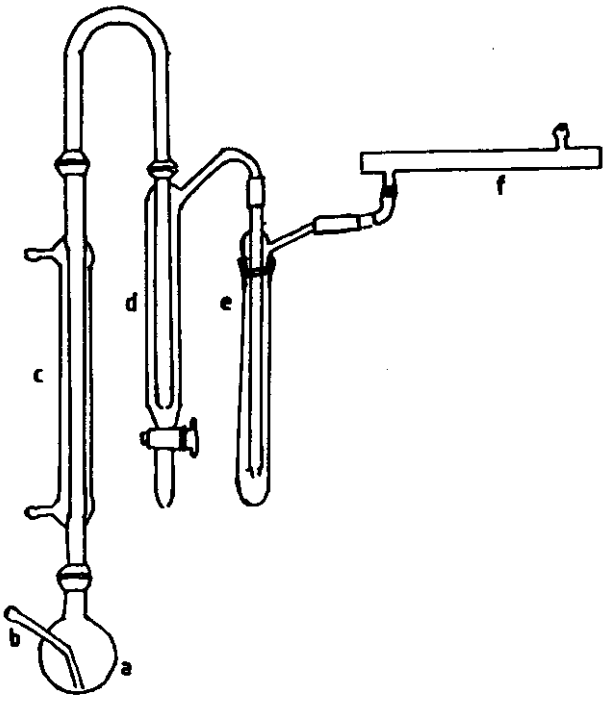

Fig.1: Apparatus for reduction of sulphate (a) reduction flask (b) N_2-delivery tube (c) condenser (d) gas washing column (e) drying tube (f) optical cell.

with a stream of nitrogen passed through it. The colourlesss mixture thus obtained was cooled with the nitrogen stream still passing and then stoppered and stored in a dark place.

Sulphate solution

For calibration purpose 1000 ppm sulphate solution was prepared by dissolving appropriate amount of potassium sulphate dried at 105°C in 1000 ml. of water.

Gas wash solution

Dissolved 10g of sodium dihydrogen phosphate 2-hydrated and 10 g of pyrogallol in 100 ml of sulfur free distilled water.

Calcium chloride was used as drying agent for the released hydrogen sulphide.

Procedure

Aliquots of the potassium sulphate solution containing 10-50 ug of sulphate was transferred to the reduction flask (a) and heated to dryness. After cooling, 3 ml of the reduction mixture were added and the flask was connected to the assembly (Fig.1). The mixture was heated to boiling for five minutes while nitrogen gas was passing through the apparatus. The released hydrogen sulphide was swept through the optical cell (f) and absorption was measured at 203 nm. The peak area calculated for different sulphate standards was plotted against the corresponding sulphate concentrations to get the calibration graph (Fig. 2).

The samples were treated as in the calibration and the sulphate content was calculated from the graph.

Results and Discussion

Table 1 lists the results of sulphate determined from synthetic samples, both by the described and the methylene blue method. The precision

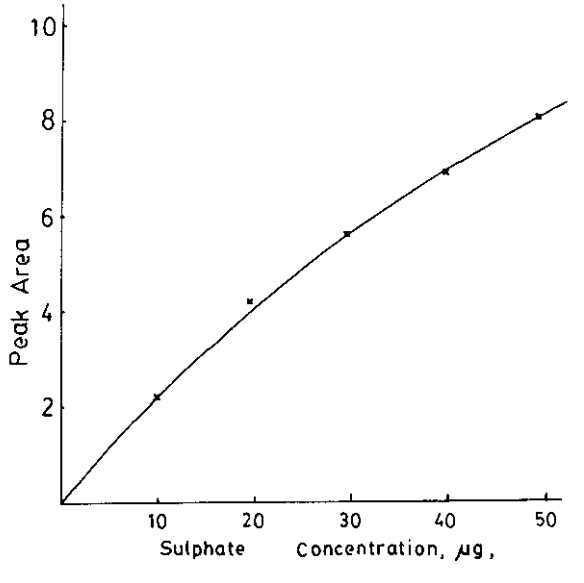

Fig.2: Calibration graph for sulphate determination

Table-1: Determination of sulphate in synthetic samples

S.No.	SO_4"present	Methylene blue method		Described Method	
		$SO"_4$ Found	% Recovery	$SO"_4$ Found	% Recovery
	µg/ml	µg/ml		µg/ml	
1.	2.00	2.10	105	2.10	105
2.	2.00	1.96	98	2.05	102
3.	2.50	2.45	98	2.44	98
4.	2.50	2.50	100	2.48	99
5.	3.00	3.12	104	3.0	100
6.	3.00	3.10	103	3.05	101
	Avg ± RSD		101.3±2.8		100.8±2.2

of the former method is much better compared to the methylene blue method. The minimum determinable concentration of sulphate by the described method is 10 ug. At values lower than this the noise-to-signal ratio becomes quite high, thus making the results less reliable. Samples containing lower values of sulphate were taken in larger quantities and evaporated to dryness before analysis.

Blank run

When a sample containing 50 ug of sulphate was analysed repeatedly, it was observed that the first three measurements showed an increasing signal which then became constant for the further measurements. This problem was eliminated when the apparatus was conditioned by boiling 3+3 ml of the reduction mixture with a small amount of sulphate for at least fifteen minutes before starting the actual analysis. This sort of blank run was required when the apparatus was being used for a new analysis. Moreover, due to the blank run the gas wash solution becomes saturated with hydrogen sulphide and the subsequant measurements were not effected to any extent.

Optimization of the system parameters

Different volumes of reduction mixture were used for reduction of a 50 ug of sulphate sample. Reduction remains incomplete when a volume less than 2 ml of the reduction mixture was used. 3 ml was selected as the optimum volume for reduction purpose. The reduction is normally completed within five minutes but this was taken as the optimum reduction time.

To select an optimum flow rate nitrogen was passed at different speeds and it was observed that an average flow by which the generated hydrogen sulphide passes through the absorbance cell within about three minutes, gives an ideal determination. Flow

Table-2: Recovery of hydrogen sulphide from sulphate samples

S.No.	SO''_4 Present µg	H_2S Present µg	Direct Method H_2S Found µg	% Recovery	Through absorbance in $Zn(CH_3COO)_2$ soln. H_2S Found µg	% Recovery
1.	10	3.96	3.50	88	2.90	73
2.	10	3.96	3.40	86	3.00	76
3.	10	3.96	3.40	86	3.30	83
4.	50	19.79	18.00	91	15.00	76
5.	50	19.79	17.00	86	14.50	73
6.	50	19.79	17.50	88	14.50	73
7.	100	38.00	35.00	92	30.00	79
8.	100	38.00	33.00	87	28.50	75
9.	100	38.00	33.20	87	29.20	77
	Average Recovery			88%		76%

Table-3: Interference from twenty fold excess of anions in the determination of 50 ug of sulphate in synthetic samples

Interferent	SO''_4 Found	% Error
Cl'	50.0	0.0
ClO'_4	50.2	+0.4
IO'_3	50.2	+0.4
$C_2O''_4$	50.0	0.0
NO'_3	49.5	-1.0
PO'''_4	50.3	+0.6
F'	49.5	-1.0
NO'_2	48.5	-3.0
$S_2O''_3$(50 ppm)	69.0	+38.0
SO''_3(ppm)	88.0	+66.0

rates greater than this produced splashing in the reduction flask, a very low flow rate of reduction was avoided because of the time factor.

In a previous paper [5] a magnesium lamp at 200 nm was recommended for the determination of hydrogen sulphide by gas-phase molecular absorption spectrometer. In the present studies a selenium hollow cathode lamp at 203 nm was found more sensitive. So all measurement were made using selenium lamp as the light source.

Recovery of sulphate (The yield of reudction)

To check the percentage recovery of sulphide from the sulphate samples, analysis of samples containing 50, 30 and 10 g of sulphate was carried out and the yield of reduction was determined by comparing the absorbance signal from known quantities of sulphate with those obtained by known

Table-4: Determination of solubility of barium sulphate in brine solution of different concentrations

S.No.	NaCl Conc.(M)	Solubility (10^{-5}M) Described Method	Spectro-photometric Method
1	0.5	5.10	5.60
2.	0.5	4.98	5.22
3.	0.5	5.15	5.25
4.	1.0	8.80	8.37
5.	1.0	8.75	8.60
6.	1.0	8.95	9.00
7.	2.0	12.07	11.93
8.	2.0	12.90	12.45
9.	2.0	11.68	12.50

quantities of sulphide. The latter determinations were performed on freshly prepared and standardized solutions of sodium sulphide [5]. Results in table 2 show that the yield of reduction is reasonably adequate, well within the experimental erros.

Lower results were achieved when the hydrogen sulphide evolved after reduction of sulphate was first absorbed by zinc acetate solution and then released by addition of hydrochloric acid for absorbance studies.

Interference of foreign ions

As reported previously [6] certain ions when present interfere strongly in the determination of sulphate by spectrophotometeric method. However, these interferences were reduced greatly by the use of the described method. A twenty-fold excess of the interferents was added to 50 µg of sulphate, and the effect is shown in table 3. Only sulphite and sulphate had a pronounced effect, certainly because of producing extra hydrogen sulphide due to their own reduction.

It was also noticed that the absorbance remains almost constant when same amount of sulphate taken from different sources is analysed.

Sulphate in Barium sulphate solubility samples

Measurement of solubility of barium sulphate in brine solutions is difficult, especially when barium is determined. This is becase of the high sodium content which interferes in barium determination by methods like atomic absorption etc. Samples from solubility

cell were filtered through a millipore filter (0.45 um) and evaporated to dryness in the reduction flask. Presence of large amounts of chloride did not interfere and the solubility results achieved are quite comparable to those achieved through barium determination by spectrophotometric method [7] (table 4). The latter method is considered suitable for barium determination in the presence of high concentrations of other ions.

Conclusion

The described method is equally useful for solid and liquid samples containing micro levels of sulphate. Most of the interferences which had been experienced by other methods of sulphate determination can be depressed by the described procedure. As compared to other methods the present method is fast enough and can be easily employed for routine analysis.

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