Spectrophotometric Determination of Sulphide by the Liberation of Dithizone from Mercury (II)-Dithizonate

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Summary: A simple and sensitive indirect spectrophotometric method is described for sulphide determination. The method is based on the reaction of mercury(II)-dithizonate with sulphide ions. Absorbance of liberated dithizone was measured at 620 nm. Effects of various parameters and interferences due to other ions have been checked. The method has been employed for a number of synthetic and sewage water samples.

Introduction

Sulphides are usually produced by the bacterial action on sulphates present in sewage waters and sediments. Under slightly acidic conditions and at elevated temperatures sulphides release hydrogen sulphide which is an undesirable atmospheric pollutant due to its unpleasant smell and toxic effects. Hence sulphide is often determined in air, water and sediment samples.

Sulphide can be determined by a number of spectrophotometric methods. The Methylene Blue method has been thoroughly investigated and most commonly used for sulphide determination in a large variety of samples [1-3]. The Ethylene Blue modification has increased the sensitivity of the original method significantly [4]. A few indirect methods for sulphide determination have also been reported. One of such methods is based on the absorbance of dithizone released when chloroform solution of silver-dithizonate is shaken with aqueous solution of sulphide [5]. In another such method absorbance of chloranilate, released from mercury(II)-chloranilate, is taken as a measure of sulphide concentration [6].

These methods are sensitive enough but certain problems are associated with them such as lengthy and combersome procedures, unavailability and instability of the reagents and lack of reproducibility. An indirect method developed in authors' laboratory is based on the absorbance of iron(III)-thiocyanate formed when mercury(II)-thiocyanate solution is reacted with sulphide ions in presence of iron(III) ions [7]. Present method for sulphide determination is based on the displacement of dithizone from mercury(II)-dithizonate complex by sulphide ions. Absorbance of released dithizone, in organic phase, is measured at 620 nm.

Experimental

Equipment

A Pye Unicam SP 8-400 double beam UV/Vis Spectrophotometer with 10 mm glass cells was used for absorbance measurements.

Standard Sulphide Solution

To prepare 1000 $\mu g\ ml^{-1}$ solution, 4.006 g of hydrated sodium sulphide (containing 60% sodium sulphide determined iodimetrically) were dissolved in 1000 ml of water. Dilute solutions of sulphide were prepared by diluting this stock solution.

Dithizone Solution

Dithizone solution 0.02% was prepared by dissolving 0.05 of the solid reagent in 250 ml carbon tetrachloride. The solution was purified with aqueous ammonia solution [8].

Mercury(II) Solution

To get 100 $\mu g\ ml^{-1}$ solution of mercury(II), 0.1620 g of A.R. grade mercury(II) nitrate was dissolved in 50 ml of 2M nitric acid and the contents were diluted to 1000 ml with water.

Mercury(II)-Dithizonate Reagent

10 ml of 100 $\mu g\ ml^{-1}$ mercury(II) solution were mixed with 50 ml of 2% sulphuric acid in a 250 ml separating funnel. The contents were shaken for two minutes with 25 ml of 0.02% dithizone solution and the light-orange coloured organic phase was separated. The extraction procedure was repeated with another 25 ml dithizone solution and the combined extract was stored in an amber-glass bottle under a layer of 2% sulphuric acid.

Calibration

In a series of ten 100 ml separating funnels, 5 ml of mercury(II)-dithizonate solution was mixed with 5 ml of 2% sulphuric acid. The mixture was diluted with 20 ml water. Then accurately measured, 0.1-1 ml aliquots of 10 $\mu g\ ml^{-1}$ sulphide solution were added in the funnels. The contents were shaken thoroughly for two minutes. After keeping undisturbed for another minute the organic phase of each funnel was separated in a series of 10 ml flasks. Volume was made up with carbon tetrachloride. Absorbance of each flask was measured against a compensatory blank at 620 nm. To get calibration, absorbance values were plotted against sulphide concentration.

Results and Dicussion

Mercury ions in an acid medium react with dithizone to form orange-yellow mercury-dithizonate, $Hg(HDz)_2$, which is soluble in carbon tetrachloride and which is the basis of a sensitive spectrophotometric method for mercury [9]. The proposed method for sulphide determination is based on the displacement of dithizone from mercury-dithizonate complex by shaking the complex solution of sulphide ions at pH 3-5. Absorbance of released dithizone, present in organic phase, was measured at 620 nm. Absorbance values were plotted against sulphide concentration.

As shown in Fig. 1, a linear calibration, with a little intercept along y-axis, was obtained for 1-10 μg of sulphide. In present work absorbance was measured against a compesatory blank. With carbon tetrachloride, using as blank, however, the intercept along y-axis was increased significantly. The

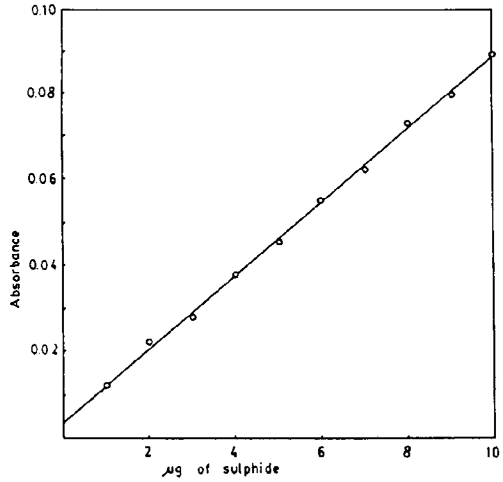

Fig. 1: Calibration for sulphide

Table 1: Effect of diverse ions on sulphide determination.

Anion added	Added as	Concentration of anion	Absorbance obtained by 10 μg $S^{=}$	Cation added	Added as	Concentration of cation	Absorbance obtained by 10 μg $S^{=}$
Nitrite	Sodium	100 ppm	0.082	Potassium	Nitrate	100 ppm	0.084
Chloride	Sodium	10 ppm	0.110	Calcium	Acetate	100 ppm	0.086
Nitrate	Sodium	100 ppm	0.085	Zinc (II)	Acetate	100 ppm	0.080
Acetate	Sodium	100 ppm	0.079	Lead(II)	Acetate	10 ppm	0.052
Sulphate	Sodium	100 ppm	0.080	Nickel(II)	Acetate	100 ppm	0.078
Sulphite	Potassium	100 ppm	0.085	Copper(II)	Acetate	5 ppm	0.036
Bromide	Potassium	10 ppm	0.123	Aluminium (III)	Nitrate	100 ppm	0.088
Carbonate	Sodium	100 ppm	0.077	Silver (I)	Nitrate	5 ppm	0.048
Thiosulphate	Sodium	100 ppm	0.083	Ammonium	Nitrate	100 ppm	0.082
Bicarbonate	Sodium	100 ppm	0.078	Iron(II)	Sulphate	100 ppm	0.079

Absorbance obtained by 10 μg sulphide as Na_2S was 0.081.

calibration graph remained linear as the sulphide concentration was less than 60 μg in the described procedure.

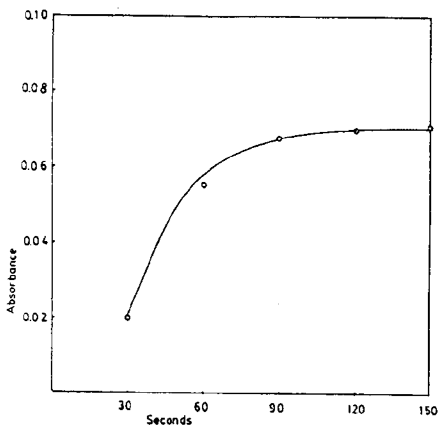

Fig. 2: Effect of shaking time

Effect of pH and Shaking Time

Effect of pH on decomposition of mercury-dithizonate by sulphide ions was checked by varying the pH from 0.1 to 6 with dilute sulphuric acid. The optimum pH range for this purpose was 3-5. At higher pH values (pH 5) low and irreproducible results have been found whereas at very low pH (pH) compensatory blank has shown significant absorbance.

Effect of shaking time was checked by shaking the contents for different intervals of time. As shown in Fig. 3, in first ninety seconds absorbance vlaues were considerably increased with shaking time. After that, however, increase in shaking time did not affect the absorbance values to any significant extent. Hence in the described procedure two minutes shaking of the contents at pH 3-5 has been recommended.

Interferences Due to Diverse Ions

To check the possible interferences, a certain quantity of sulphide has been determined in presence of a number of other common ions. The anions were added as their sodium, potassium and ammonium salts whereas the cations were employed in the form of acetates and nitrates. The results obtained in the presence of diverse ions in different concentrations are summarized in Table 1.

Among the anions interferences were observed due to chloride and bromide as expected. These ions increased the absorbance due to free dithizone and higher results of sulphide determination were obtained. This is mainly due to the fact

Table 2: Comparison of results for analysis of some sulphide samples.

Samples	No. of determinations		Average amount of S" found (μg/ml)	
			by described method	by Ethylene blue method
Synthetic Samples (H2S passed through 0.001M zinc acetate solution)	1	5	33.2	37.4
	2	"	78.5	71.6
	3	"	45.0	49.4
	4	"	38.2	39.0
	5	"	75.2	71.5
	6	"	66.0	68.2
Sewage Water Samples	1	3	42.0	40.2
	2	3	55.2	59.0
	3	5	43.5	42.5
	4	5	57.8	44.0
	5	3	48.2	49.7
	6	5	52.4	55.6

that chloride and bromide ions also react with mercury(II)-dithizonate complex to form respective mercury(II)-halide and release dithizone. Among the cations, however, lead, copper and silver interfered the determination by giving lower sulphide results probably due to formation of stable insoluble sulphides of these metals. Rest of the anions and cations showed negligible effect on the determination.

Sulphide in Samples

Sulphide content has been determined by the proposed method as well as by Ethylene Blue Method [4] in synthetic and sewage water samples. Sewage water samples, collected from various places of the city*, were filtered prior to analysis and analysed without dilution. The synthetic samples were prepared by passing hydrogen sulphide through 0.001M zinc acetate solution. Different volumes of diluted colloidal suspension of zinc sulphide were analysed by the both methods.

As it can be seen from Table-2, the results of sewage water samples obtained by both methods are not very different from each other. However, in the case of zinc sulphide suspension the difference in certain cases is noticeable which may be attributed to the hetrogenity of the samples.

Conclusion

The described method proved itself a simple, low cost and reasonably accurate method for the estimation of minute quantities of sulphide. Though a few ions interfere but these can be eleminated before sulphide determination. The method is equally useful for insoluble sulphides as well as for soluble sulphides.

References

1. P.K. Zutshi and T.N. Mahadevan, *Talanta,* **17,** *1014 (1970)*
2. K. Hofmann and R.Z. Hamm, *Anal. Chem.* **232,** *167 (1967).*
3. Z. Marczenko, Spectrophotometric Determination of Elements Ellis Harwood Ltd. Chichester, 1976, page 506.
4. T.D. Rees, R.A. Gyllenspetz and A.C. Docherty, *Analyst;* **96,** *201 (1971).*
5. W.J. Kristen, *Mikrochim, Acta, 1086, (1955).*
6. R.E. Humphrey and W. Hinze, *Anal. Chem.* **43,** *1100 (1971).*
7. J. Anwar and Amtul-Aziz, *J. Chem. Soc. Pak.* **10,** *351 (1988)..*
8. Ref. 3 page 492.
9. H. Friedeberg, *Anal.Chem.*, **27,** 305 (1955).

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