

Spectrophotometric Determination of Sulphide in Non-polar Media by the Mercury(II) thiocyanate Reaction

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Summary: A simple, rapid and accurate method for the spectrophotometric determination of sulphide in non-polar media is described. The method is based upon the reaction of mercury(II) thiocyanate with sulphide to release thiocyanate which reacts with iron(III) to form iron-thiocyanate. The reaction is performed in non-aqueous medium. Cyclohexane and iso-octane are used as organic solvents separately. The effects of a number of parameters like time, temperature, concentration of reagents and diverse ions are investigated. The method has significant potential of determining sulphur in sulphur containing organic compounds.

Introduction

A number of spectrophotometric methods for determining sulphide in aqueous media has been reported in literature [1-3]. By these methods trace quantities of sulphide has been determined in air [4], water [5], plant materials [6], soils [7], and biological materials [8]. Methods for the determination of various forms of sulphur in organic matrices could also be found in literature. Bartlett and Skoog [9] estimated free sulphur in hydrocarbons by a method based on the formation of iron(III) thiocyanate. Toenniss and Bakay [10] determined organic sulphur in nucleoproteins by barium sulphate turbidity method. Hastings and Johnson [11] used ultraviolet absorption spectroscopy for determining aliphatic sulphides in hydrocarbons. Though these methods are sensitive enough for trace quantities of sulphur but precision is always suffered by the lengthy and cumbersome procedures and potential interfering species present in the sample.

The work reported here describes a simple and accurate method for the determination of sulphide sulphur in non-polar media. The method is

based on the displacement of thiocyanate by sulphide. The released thiocyanate reacts with iron(III) to form iron(III) thiocyanate complex which is determined spectrophotometrically. The reaction is performed in non-aqueous media. Cyclohexane and iso-octane are used as solvents independently.

Experimental

Equipment

A Pye Unicam SP 8-400 UV/VIS double beam spectrophotometer with 10mm quartz cells is used for absorbance measurements.

Thiocyanate Solution

For mercury(II) thiocyanate solution, 95 mg of the AnalaR Grade salt was dissolved in 200 ml of absolute ethanol. After complete dissolution the contents were diluted to one litre to get 3×10^{-4} M solution. The solution was stored in an amber-glass bottle and used throughout the work.

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Iron(III) Solution

For iron(III) reagent, 8.08 g of AnalaR Grade iron(III) nitrate was dissolved in 100 ml of 5M perchloric acid to obtain 0.2M solution of iron(III). This solution was also stored in dark.

Standard Sulphide Solution

For the sulphide standard solution, 102 mg of hydrated sodium sulphide (containing 60% assay determined iodimetrically) was dissolved in 250 ml of absolute ethanol to get $100 \mu\text{g ml}^{-1}$ ($3.13 \times 10^{-3}\text{M}$) sulphide solution. This stock solution was appropriately diluted with ethanol before use.

Calibration Procedure

Transfer 10 ml of absolute ethanol into a set of five 25 ml volumetric flasks. Add 3.5 ml of 3×10^{-4} mercury(II) thiocyanate solution followed by aliquots of sulphide solution containing 5- 25 μg of sulphide in the flasks. Add 0.5 ml of 0.2M iron(III) nitrate solution followed by 8 ml of isooctane or cyclohexane. Mix the contents gently and keep the flasks for five minutes to develop the colour.

Dilute the contents to the mark with ethanol. Prepare a compensatory blank by mixing the reagents except sulphide solution. Measure the absorbance at 507 nm using compensatory blank as reference. To prepare calibration, plot the absorbance values against sulphide concentration.

Results and Discussion

An indirect spectrophotometric method for the determination of sulphide in aqueous media based on the reaction of iron(III) with the liberated thiocyanate ions has already been reported [12]. In present work the method has been extended to non-polar media such as ethanol-isooctane or ethanol-cyclohexane. A linear calibration in the range of $0.2 - 2 \mu\text{g ml}^{-1}$ sulphide, shown in Fig. 1, is obtained by the described procedure.

The absorption maxima of iron(III) thiocyanate complex in aqueous media is at 480 nm [13] but in ethanol and isooctane or cyclohexane it is found at 507 nm, hence all the absorption measure-

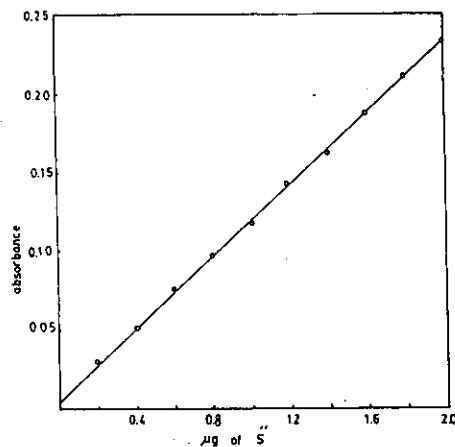


Fig. 1 Calibration of sulphide

ments in this work have been made at this wavelength. The relative standard deviation calculated for ten measurements of $1.5 \mu\text{g}$ sulphide was 2.2%.

Effect of Reagents Concentration

It has been observed that in non-polar media such as ethanol-isooctane or ethanol-cyclohexane; relatively lower concentrations of the reagents than aqueous media are required to obtain the maximum absorbance. Higher concentrations of the reagents especially of iron(III) did not cause any net increase in the absorbance, as shown in Fig. 2, but simply enhanced the absorbance of the compensatory blank. Similarly 3 ml of thiocyanate solution

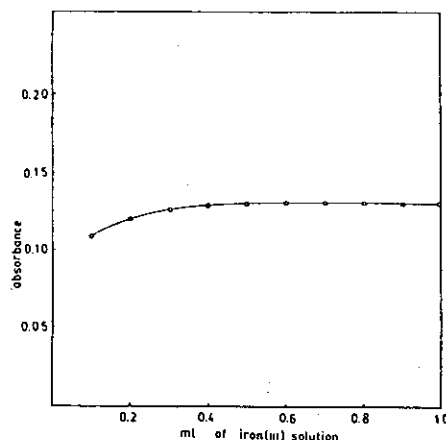


Fig.2: Effect of iron(III) solution concentration.

was enough to get the maximum absorbance for 5-25 μg of sulphide. Higher concentrations of thiocyanate solution, as revealed by Fig. 3, depressed the final absorbance significantly, probably due to the fact that sulphides of mercury and cadmium are formed preferably in dilute solutions.

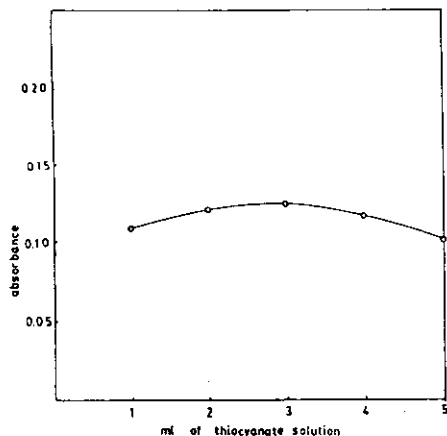


Fig.3: Effect of Thiocyanate solution concentration

Effect of Organic Solvents

Two organic solvents, isooctane and cyclohexane were employed in this work. The optimum volume found in both cases was 8ml. More than 8 ml isooctane gave an immiscible layer in the system whereas more than 8 ml of cyclohexane depressed the absorbance considerably. Hence in the procedure addition of 8 ml organic solvent is recommended. These solvents have already been used for chloride estimation by this principle [14]. Absolute ethanol is used as a major solvent to blend isooctane or cyclohexane and inorganic acid present in the system.

Effect of Time and Temperature

Effect of time on the final absorbance due to iron(III) thiocyanate complex has also been checked. As it is clear from Fig. 4, the absorbance decreased slowly in the first fifteen minutes after which it dropped sharply. After an hour the absorbance was only one tenth of that in start. This reveals that iron (III) thiocyanate does not retain its stability for longer periods of time in a solvent system such as used in this work. However absorbance measurements in first ten minutes after mixing the reagents gave reproducible results.

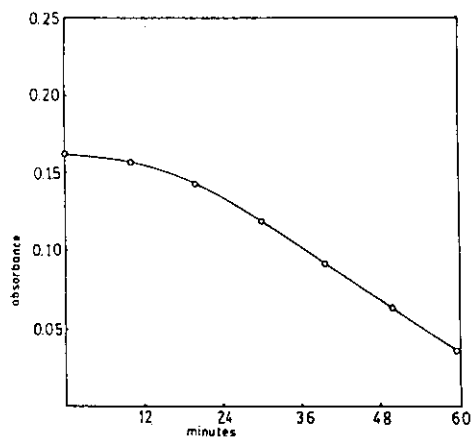


Fig.4: Effect of time on absorbance

Absorbance of sulphide containing sample was also measured at elevated temperatures. The results shown in Fig. 5, revealed that no appreciable change appeared in the absorbance when the contents were heated up to 80°C.

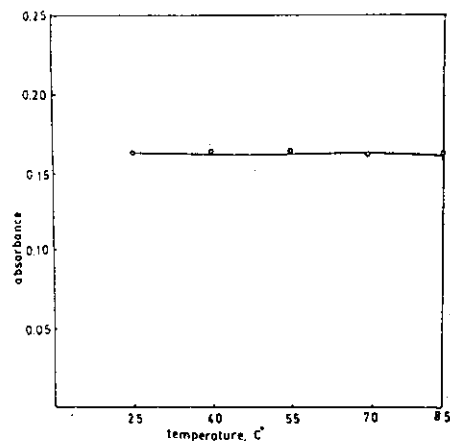


Fig.5: Effect of temperature on absorbance.

Effect of Order of Mixing the Reagents

As shown in Fig. 6, a pronounced effect in the final absorbance has been observed by changing the order of mixing the reagents. The maximum absorbance was found in the case when thiocyanate solution was added into ethanol followed by the sulphide sample. Then the iron(III) solution was added and at the last cyclohexanone was mixed. Contrarily the minimum absorbance was observed when sulphide was added to iron(III) solution present in ethanol and then thiocyanate solution

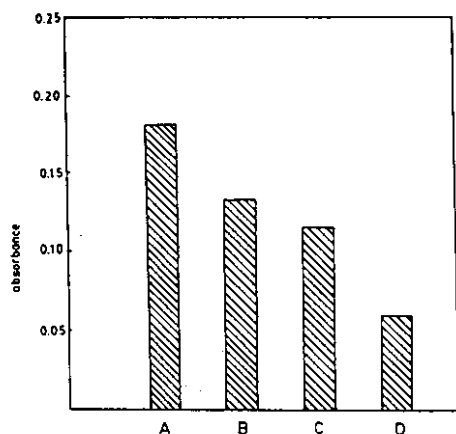


Fig.6: Effect of order of mixing the reagents

- A: - Ethanol + thiocyanate + sulphide + Iron (III) + Cyclohexanone
 B: Ethanol + sulphide + thiocyanate + Iron(III) + Cyclohexanone
 C: Ethanol + Iron (III) + thiocyanate + sulphide + Cyclohexanone
 D: Ethanol + Iron (III) + sulphide + Thiocyanate + Cyclohexanone

was mixed before adding cyclohexane. This indicates that when sulphide is already present alongwith iron(III) in ethanol, displacement of thiocyanate ions from incoming mercury(II) thiocyanate is not completed.

Effect of Other Ions

To check the effect of various anions and cations on the determination of sulphide by the described procedure, saturated solution of the ions

in absolute ethanol was used. The anions were added as their salts of sodium and potassium and cations were mixed as their nitrates.

As shown in Table-1, among the anions, chloride, bromide and thiosulphate interfered the determination and yielded significantly higher results of sulphide. This is due to the fact that like sulphide these ions also react with mercury(II) thiocyanate to displace thiocyanate ions which form iron- thiocyanate complex. As for as cations are concerned only lead and copper gave lower results due to the formation of insoluble sulphides whereas other cations showed negligible effect on the determination.

Response of Sulphur Containing Organic Compounds.

It has been observed that sulphur containing organic compounds such as thiourea, allyl thiourea and aminothiazole etc. also give a similar response as found for inorganic sulphide ions. But the solutions of different compounds, containing equal quantities of sulphur, gave different absorbance values. This indicates that response of each compound is slightly different. As shown in Table-2, results obtained for thiourea are less and that obtained for allyl thiourea are slightly greater than that obtained for equimolar sodium sulphide. This is probably due to the difference in the reactivity of various compounds. The results obtained for aminothiazole and mercaptosuccinic acid are almost same as given by sodium sulphide.

Table-1: Effect of other Ions on the Sulphide Determination

Anion	Added as	S' found $\mu\text{g}/25\text{ ml}$	Cation	Added as	S' found $\mu\text{g}/25\text{ ml}$
Acetate	Sodium	30.2	Ammonium	Nitrate	29.6
Nitrite	"	31.0	Calcium	"	30.2
Nitrate	Potassium	30.5	Lead	"	22.2
Chloride	Sodium	38.2	Zinc	Acetate	30.0
Thiosulphate	"	36.0	Chromium	"	28.9
Phosphate	"	29.8	Iron	Sulphate	29.7
Sulphate	"	29.8	Nickel	"	28.6
Bromide	Potassium	42.5	Copper	"	24.2
Carbonate	Sodium	30.2	Magnesium	"	30.6

Sulphide used $30\mu\text{g}/25\text{ ml}$ as Sodium Sulphide.

Table-2: Response of Sulphur Containing Organic Compounds

Sulphur containing compound	Sulphur	
	Taken $\mu\text{g}/25\text{ ml}$	Found $\mu\text{g}/25\text{ ml}$
Sodium Sulphide	(Used as standard)	30.0
Thiourea	30	26.2
Allyl Thiourea	30	35.5
2-Aminothiazole	30	31.8
Mercaptosuccinic acid	30	32.2

This suggests that the described method can be used for the estimation of sulphur in the compounds like aminothiazole by using sodium sulphide as standard, however for the compounds giving different results such as thiourea one has to use the same compound as standard.

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