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DETERMINATION OF SULPHIDE IN THE PRESENCE OF SULPHITE AND THIOSULPHATE

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A spectrophotometric method for the determination of sulphide in the presence of sulphite and thiosulphate has been developed. In this method sulphide when treated with selenium dioxide in the presence of gelatine gives a yellow colour which shows maximum absorption at 340 nm. The interference due to sulphite and thiosulphate has been studied. The maximum error was 2.6 % when a 10 μg sample of sulphide was analysed in the presence of 5 μg of sulphite. The method is convenient, precise and accurate.

Key words: Spectrophotometric, Sulphide, Selenium dioxide.

INTRODUCTION

Numerous methods are available in literature for the determination of sulphide. Among titrimetric methods, the oldest method is based on the reaction of H_2S with iodine to give elemental sulphur [1]. This method does not give accurate results because in acidic medium H_2S has a tendency to escape. Another method is based on the reaction of sulphide with iodine in basic medium to give sulphate. Then the excess of iodine is back titrated with thiosulphate [2]. Sulphide determination has also been carried out via formation of cadmium sulphide and zinc sulphide [3-4]. The excess of acidic iodine is then added to the precipitate followed by back titration. Titrimetric determination of sulphide in the presence of sulphite and thiosulphate was accomplished by selectively precipitating sulphide as cadmium and Zinc sulphide [5-10] while sulphite and thiosulphate were determined from the filtrate. The Wollak method [11] is very important for the determination of sulphide, sulphite and thiosulphate in presence of each other. In this method the total amount of the three ions is determined iodometrically in one aliquot. To another aliquot zinc acetate is added; the sulphite is masked with formaldehyde, and iodine is added to the solution, which still contains the zinc sulphide precipitate. Back-titration of the excess of iodine gives the total amount of sulphide and thiosulphate. Thiosulphate was determined from the third aliquot by carefully oxidizing it with iodine. The excess of iodine is removed by the addition of Na_2SO_3 to a colourless end-point. The accuracy of the method becomes doubtful where filtration of a precipitate is often unsatisfactory because the adsorption of other ions can

take place on the precipitate. This method, in fact, does not give accurate results for the determination of thiosulphate. In another method sulphide is determined by evolving the H_2S gas with the help of a weak acid and then absorbing the gas in iodine solution, the excess of which can be titrated with thiosulphate [12-13]. Kolthoff determined sulphide with permanganate in alkaline medium and used iodometric back titration of the excess [14]. But the other sulphur containing compounds interfered in the procedure. Mixtures of sulphide, sulphite and thiosulphate were also titrated with sodium nitrite solution in mildly acidic medium with chloroform and a trace of potassium iodide as indicator [15]. Periodate was determined separately. Sarwar and others used *N*-bromosuccinimide for the volumetric determination of sulphide but other sulphur contaminants interfered [16].

Among the instrumental methods of analysis the polarographic method is applied most widely for the determination of sulphide [17-19]. A spectrophotometric method based on the reaction of amino-*N*, *N*-dimethylaniline and ferric chloride in the presence of hydrogen sulphide to give Methylene Blue [20] was developed. The colour so developed was measured spectrophotometrically. With this method microgram quantities of sulphide could be determined. The conditions of this method were very critical. *p*-Phenylenediamine has also been used for the determination of sulphide which forms a purple colour which was measured spectrophotometrically [21].

Sodium nitroprusside reacts with sulphide in alkaline medium to give a violet complex which can be measured spectrophotometrically [22]. Another colour reaction between Hg-diphenylcarbazone and sulphide ions was used for the spectrophotometric determination of sulphide

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[23]. This method needs stringent control of conditions making it rather tedious and time consuming.

In the present investigation a spectrophotometric method has been described. It is based upon the reaction of sulphide with selenium dioxide. The method is simple, convenient, reasonably accurate and rapid.

EXPERIMENTAL

Apparatus

1. Spectronic 20 Bauch and Lomb spectrophotometer was used in this investigation.. [2]. Beckman pH meter was employed for all pH measurements. [3]. Microburette and micropipettes were used for taking definite volumes.

Reagents

1. *Sodium sulphide* (BDH): Solution was prepared in distilled water and standardized [1].

2. *Sodium sulphite* (E. Merck). Solution was prepared in distilled water and standardized [2].

3. *Selenium dioxide*. A 1 % solution of the reagent was prepared in distilled water.

4. *Gelatine*. A 0.5 % solution was prepared in hot distilled water.

Procedure

For the direct spectrophotometric determination of sulphide, 1 ml of the test solution containing a definite amount of sulphide was taken. To this was added 3 ml of 1 % selenium dioxide solution followed by 6 ml of 0.5 % solution of gelatine. The resulting contents were then diluted to 15 ml with distilled water and then heated for 5 min. at 100°, cooled under tap water and then again made up to 15 ml with distilled water. The resulting yellow colour was measured at 340 nm. A calibration graph was then prepared by taking different amounts of standard sulphide solutions. It obeyed Beer's law (Fig. 1). The unknown samples were then read from the same graph.

RESULTS AND DISCUSSION

It can be seen from the results of Tables 1, 2, and 3 that sulphide can be determined quite precisely and accurately using selenium dioxide. The limits of tolerance of sulphite and thiosulphate in the determination of sulphide have also been determined.

It has been observed that sulphide can be determined in the presence of sulphite and thiosulphate when they are present in 1/5th the amount of sulphide. The results can be seen in Tables 1 to 3. It is clear that for a 10 µg sample

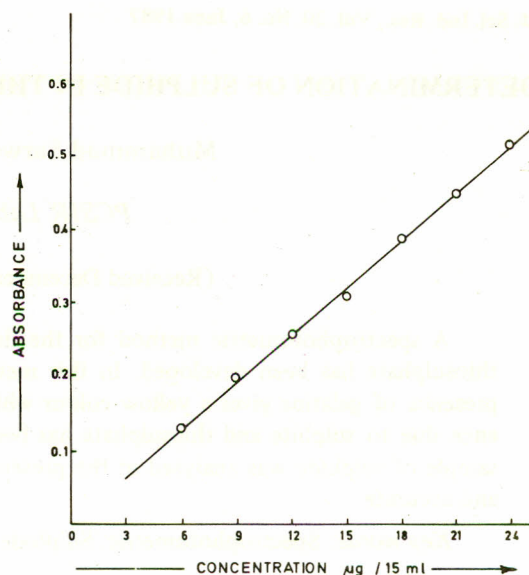


Fig. 1. Calibration curve.

Table 1. Determination of sulphide

Amount taken (µg)	Amount found (µg)	Rel. Std. Deviation (%)
10.0	9.9	1.6
12.2	12.1	1.2
13.4	13.3	1.4
13.8	13.7	1.0
15.7	15.6	0.8
16.1	16.0	0.8
17.5	17.4	0.7
18.0	17.9	0.5
19.4	19.4	0.5
20.1	20.0	0.5

Every value determined represents the average of five determinations.

Table 2. Determination of sulphide in the presence of sulphite

Amount taken (µg)	Sulphite added (µg)	Amount found (µg)	Rel. Std. Deviation (%)
10.0	1.0	9.9	1.2
10.0	2.0	9.9	1.3
10.0	3.0	10.2	1.8
10.0	4.0	10.2	2.0
10.0	5.0	10.3	2.6

Every value determined is the average of five determinations.

Table 3. Determination of sulphide in presence of thiosulphate

Amount taken (μg)	Thiosulphate added (μg)	Amount found (μg)	Rel. Std. Deviation (%)
10	2	9.9	1.2
10	3	9.8	1.6
10	4	10.3	2.0
10	5	10.2	2.0
10	6	10.4	3.2

Every value is the average of five determinations.

of sulphide 2 μg of sulphite and thiosulphate do not interfere in the determination. The maximum error at this concentration is 1.0 %.

Various parameters of the reaction are discussed below.

1. *Effect of temperature on colour intensity.* The colour intensity of the reaction product was maximum at 100° and remained constant for 1 hr.

2. *Effect of the order of mixing the reagents.* The order of mixing the reagents affects the development of colour. During the study it was observed that best results were obtained when selenium dioxide was added before the addition of gelatin. However, the colour was also developed even if the reagents were mixed in reverse order but in this case a suspension was formed.

3. *Absorption spectra of the product.* The absorption spectrum of the coloured reaction product was scanned from 250 nm to 850 nm. The absorption maximum was at 340 nm.

4. *Effect of reagent concentration on absorbance.* Keeping the amount of sulphide constant the absorbance was measured at 340 nm for different concentrations of colour developing reagent. The optimum amount of SeO_2 was 30 mg/15 ml for 6 μg of sulphide for the maximum production of colour.

5. *Effect of gelatine concentration on absorbance.* The optimum concentration of gelatine for maximum colour production was 30 mg/15 ml of solution. The concentration of sulphide ranged between 6 to 24 μg .

6. *Effect of pH on absorbance.* During the investigation it was observed that pH had no effect on the intensity of colour. The pH was varied from 2 to 10 and it was

found that no appreciable change occurred in absorbance.

The reaction between SeO_2 and sulphide ends up with the formation of selenium sulphide which gives an orange-coloured fine suspension. This is stabilized with the addition of gelatine. Under such conditions sulphite does not interfere with the procedure. The effect of other anions such as thiosulphate, sulphate, chloride, bromide, nitrite, nitrate, phosphate, sulphocyanide, fluoride and cyanide has also been investigated. It has been found that these ions do not interfere with this determination. The method is reasonably precise, accurate and convenient to use.

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