

Comparative Study of Different Methods for Sulphide Determination when Adopted to Flow System

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Summary: Different FIA procedures based on spectrophotometric determination of sulphide are described. For each method the effect of various parameters including, reagent concentrations, flow rate, pFI mixing coil length, minicolumns and interfering species are investigated. Comparison of these methods with respect to detection limit, sampling rate and accuracy is made. Detection limits of 80 ppm, 1.0 ppm and 0.5 ppm with sampling rates 120, 30 and 44/hr, having the relative standard deviation 0.96, 1.8 and 0.4% respectively were observed for the three methods established.

Introduction

Sulphide is generally present in ground water, particularly in hot springs, and is common in waste waters, coming partly from the decomposition of organic matter, sometimes from industrial wastes, but most from reduction of sulphates. Hydrogen sulphide is very toxic and it attacks metal directly and indirectly has caused serious corrosion of concrete sewers since it is oxidised biologically to sulphuric acid on the pipe wall.

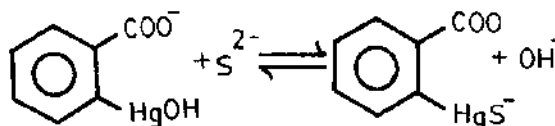
Sulphur is largely used for the production of sulphuric acid, but it is also used in the manufacture of wood pulp, carbon disulphide, rubber and various dyes, insecticides, fungicides and other chemicals. Sulphur dyestuffs fulfill a very useful purpose in cotton dyeing. They are much cheaper than vat dyes although not as fast, and they are superior to the direct dyes in all-round fastness.

Different methods are available for the determination of small quantity of sulphide in various samples. The best known are probably, the reduction of iron (III) in the presence of 1,10 phenanthroline [1], methylene blue methods [2,3], the decolorization of coloured complexes, using chloroform solutions (dilute) of copper quinoline-8-olate [4], ultra-violet absorption [5,6] and turbidimetric methods [7]. Various other reagents have been proposed for sulphide ion determination which include, the use of iodine and thiosulphate [8], the starch iodide system [9] and chromium (VI) in the presence of EDTA [10].

The use of minicolumn of chelating resin in the flow system have been elaborated for metals by atomic absorption spectrometry [11- 13]. Indirect methods often depend on the displacement of a chromogenic species from insoluble compounds [14].

In the study presented here, three different methods for sulphide determination have been adopted to FIA and compared.

In the first established spectrophotometric method (hereafter named as method 'A') for sulphide determination, organic mercury compound of the type R-HgOH, which form complexes with thiourea, xanthates, mercaptans and compounds that form ions such as S²⁻, Sx²⁻, Cs³⁻ and Cs⁴⁻ was used. This property can be used analytically for the determination of these types of sulphur containing compounds. These complexes are also soluble in water and in the presence of a suitable colouring reagent, it is possible to detect one sulphur compound in the presence of another [15]. The overall reaction between the reagents (o-hydroxymercuribenzoic acid and sulphide in the presence of sodium nitroprusside) is illustrated below and the absorbance of the complex was measured at a wavelength of 545 nm.



In the second established spectrophotometric method for sulphide (hereafter known as method 'B'), the reaction between cacotheline (nitrobruciquinone) and sulphide was studied in acidic and basic media. No reaction was observed in basic media. In acidic media, even though cacotheline was reduced to a pink product, sulphide was oxidised to sulphur, which was precipitated. Therefore the reaction was carried out in acetate buffer. Quantitative results were obtained at a pH value of 4.5. The absorbance of the product was measured at a wavelength of 510 nm.

In the third and last established method (called method 'C') a minicolumn of an ion-exchange resin in thiocyanate form is incorporated into a FIA system for sulphide determination spectrophotometrically. The reaction investigated was displacement from an ion-exchange resin of thiocyanate which is straightforward. Thiocyanate rapidly forms a red complex with iron(III) which is measured at 455 nm in a flow through spectrophotometer.

Experimental

Materials and Methods

All reagents were of analytical grade and deionised/distilled water was used throughout the established methods.

i) *o*-Hydroxymercuribenzoic Acid Solution 1×10^{-3} M.

This solution was prepared by dissolving 0.18 gm of *o*-hydroxymercuribenzoic acid in 500 ml of water containing 4 g of sodium hydroxide.

ii) Aqueous Sodium Nitroprusside Solution 0.1% (w/v).

iii) Potassium Acetate Solution 0.1 M.

A 2.45 g of potassium acetate was dissolved in water and diluted upto 250 ml in volumetric flask, and the pH 4.5 was adjusted with 1 M hydrochloric acid.

iv) Aqueous Cacotheline Solution 0.075% (w/v).

v) Ferric Chloride Solution 7.5×10^{-3} M:

This solution was prepared by dissolving 0.5 g of ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in 250 ml of water and the pH 1.6 was adjusted with 2 M hydrochloric acid.

(vi) Sulphide Stock Solution

Sodium sulphide solution was prepared fresh whenever required by dissolving 0.5 g of AnalaR $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in 250 ml of water. The crystals were initially rinsed with water. The sulphide contents was determined iodimetrically [8]. After standardization, different standards of sulphide were prepared by serial dilution of this stock solution with water.

Preparation of Ion Exchanger Column

The strongly basic anion-exchange resin "Amberlit" IRA 400 (14-52 mesh) in chloride form was used and converted to thiocyanate form as follows [16]. From the above mentioned resin 2.0 g portion was placed in a round bottom flask and shaken twice with 50 ml of 0.1 M potassium thiocyanate solution for 20 min and thrice with 50 ml of 2.0 M potassium thiocyanate solution for 20 min. The resin was filtered and washed between each shaking with water. After that resin was shaken twice for 10 min with 50 ml of water, filtered off and left for 24 hr. in water. After filtration, the different length of glass tube (2-8 cm long, 2 mm i.d) were packed. Glass wool and silicone tube were put at both ends of the glass tube to prevent movement of the resin particles by the carrier stream. When FIA system shown in Fig. 8, was used, water was passed through the exchanger glass tube, until a suitable base line was achieved, and the glass tube was stored in this condition until required for use.

Preparation of the Suppressor Column

A silver-form column was prepared from "Amberlit" IR-120 (15-52 mesh) in cationic form by passing 30 ml of 1 M silver nitrate through the column (3 cm long 2.0 mm i.d) for 30 min at a flow rate of 1 ml/min. Water was passed until a test with chloride showed the absence of silver ions in the effluent.

Apparatus

In the experimental set up shown in Figs. 1,4 and 8, the carrier streams were pumped by an Ismatec (Ragloo 100) peristaltic pump and sulphide

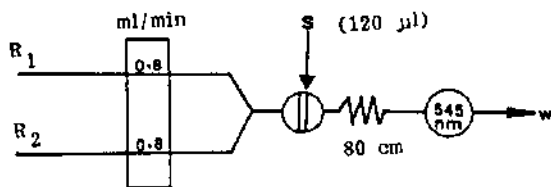


Fig. 1: Dual channel flow injection system for determination of sulphide (method A). Sample value of $25 \mu\text{l}$ of sulphide standards were injected R_1 (o-hydroxymercuribenzoic acid), R_2 (Sodium nitro-prusside).

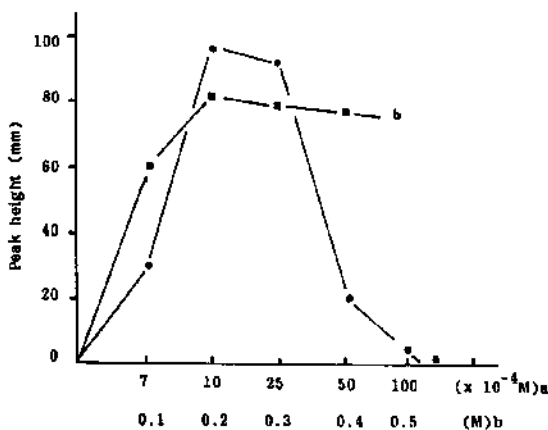


Fig. 2: a) Effect of o-hydroxymercuribenzoic acid and b) sodium hydroxide on complex formation.

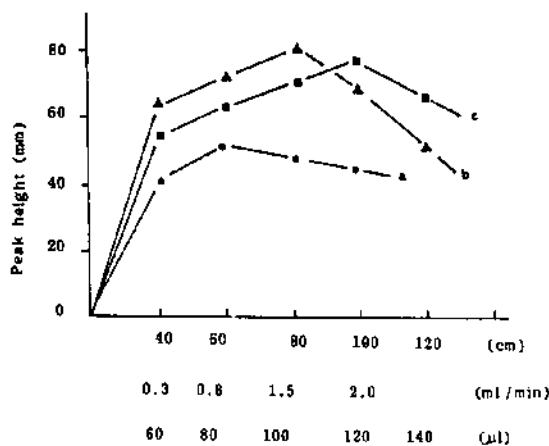


Fig. 3: a) Effect of flow rate, b) mixing coil length and c) sample volume on the response.

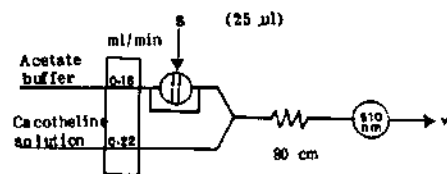


Fig. 4: Dual channel flow injection manifold for sulphide determination (used for method B).

samples of different volumes were introduced by means of a Rheodyne 5020 injection valve. Teflon tubing 0.8 mm i.d was used for all connections. A Novaspec II (LKB) flow through cell spectrophotometer, coupled with a recorder (Kipp and Zonan, BD 40) was used for absorbance measurements at different wavelengths as described in the text.

Results and Discussion

During the optimization of flow system (Fig. 1), o-hydroxymercuribenzoic acid and sodium nitro-prusside had to be taken in two streams. The mixture of these two reagents in a single stream had a deleterious effect on the peak height indicating a deterioration of reagent strength. Both of solutions were run separately and mixed before the injection point. The peaks were found to be highly reproducible.

To select the concentration level of o-hydroxymercuribenzoic acid for complex formation, different concentrations of it were used. As shown in Fig. 2, the peak height increased with increasing the concentration upto $1 \times 10^{-3} \text{ M}$ and decreased as the concentration was further increased. The o-hydroxymercuribenzoic acid solution $1 \times 10^{-3} \text{ M}$ was selected for further studies. This solution was prepared in 0.2 M sodium hydroxide (optimized, Fig. 2).

The effect of sodium nitroprusside was also investigated using various concentrations in percentage from 0.05 - 1.0 % (w/v). From 0.05 - 0.1% (w/v) a steady base-line was obtained with increasing peak height. On further increase the peak height was decreased and a non steady base line was observed. Due to this effect a solution of 0.1% (w/v) sodium nitroprusside was selected for further studies.

Figure 3, shows the effect of other parameters including, flow rate, mixing coil length and sample loop. The maximum peak height was achieved with a flow rate of 0.8 ml/min. The sensitivity decreased as the flow rate of both the streams increased. Mixing coil length covering the range 40 - 120 cm was studied. Response increased gradually as the length of the coil increased upto 80 cm and decreased on further increase. Therefore the flow rate of 0.8 ml/min and mixing coil length of 80 cm were selected for further studies in terms of the sampling rate and reagent consumption. The effect of sample loop was optimized. Samples of sulphide were injected with a sample loop of 120 μ l (0.5 mm i.d., length 60 cm), highest response was obtained and selected for other experiments.

Calibration Graph

A calibration graph for sulphide obtained under the calibrated conditions (Fig. 11) was linear over the range $3 - 11 \times 10^{-4}$ M. The limit of detection was 8×10^{-5} M (80 ppm) and the sample rate was 120/hr. The relative standard deviation was 0.96% of 10 measurements.

Method B

Various parameters have been studied for the optimization of the flow system (Fig. 4) using 5×10^{-4} M sulphide solution. The effect of flow rate in the sample carrier stream (acetate buffer) and colouring reagent stream (cacotheline) were studied from 0.16 - 0.5 ml/min. At a flow rate of 0.16 ml/min for sample carrier stream and 0.22 ml/min for coloring reagent, maximum response was achieved, on further increase in the flow rate the peak height was decreased (Fig. 5). The flow rates of both solutions (acetate buffer and cacotheline), 0.16 ml/min and 0.22 ml/min respectively were selected for further studies.

The effect of acetate buffer pH values (3.5 - 5.5) and concentration (0.01 - 1.0 M) was investigated. The results obtained are shown in Fig. 6. The optimum response at pH 4.5 and concentration 0.1 M was achieved and selected for further investigations. Deionised water was also used as a sample carrier stream but no response was obtained.

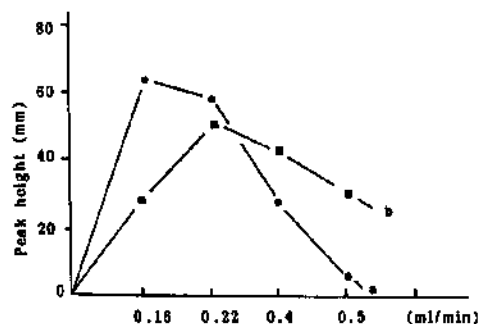


Fig. 5: a) Effect of acetate buffer flow rate in the line of sample injection and b) cacotheline flow rate on the complex formation.

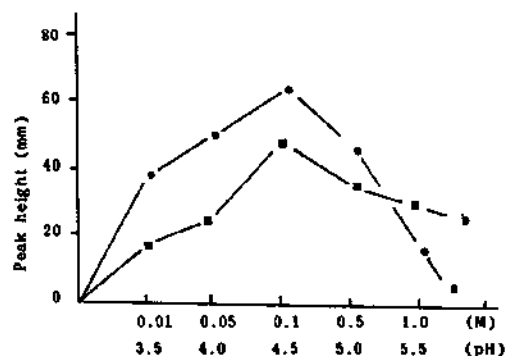


Fig. 6: a) Effect of acetate buffer concentration and b) its pH on peak height.

Fig. 7, shows the effect of colouring reagent cacotheline concentration in percentage and mixing coil length. The maximum peak height absorbance was obtained with 0.075% (w/v) cacotheline and selected for further studies. The peak height was increased using the coil length from 20-80 cm and slightly decreased on further increment. The length of mixing coil of 80 cm was used subsequently.

Calibration Graph

From the stock solution of sulphide, a series of standard solutions were treated according to the developed method under the optimum conditions. The calibration graph shown in Fig. 11, was linear upto 11×10^{-4} M sulphide. The detection limit was 1×10^{-6} M (1 ppm), and the throughput was 30 samples/hr. The relative standard deviation was 1.8% for 10 measurements.

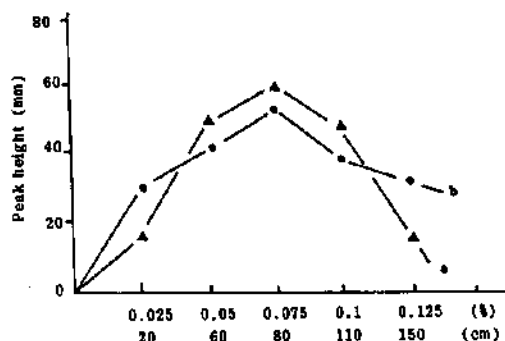


Fig. 7: a) Effect of colouring agent cacotheline and b) on mixing coil length, on the peak height.

Method C

Various experimental aspects were optimized for the dual channel manifold used (Fig.8) taking 1×10^{-4} M sulphide solution. The effect of ferric chloride in the range 7.5×10^{-4} to 1×10^{-2} M and pH values 1.2 - 2.8 were examined. As shown in Fig.9, the maximum signals were obtained at 7.5×10^{-3} M, at pH 1.6. In the solution of low pH, the concentration of chloride is also greater, so that protonation of the thiocyanate and ferric chloride complex formation may both contribute to the decrease in the concentration of iron(III)/thiocyanate complex produces and therefore the smaller signals. When the pH exceeds 1.6, hydrolysis of iron (III) become noteworthy and produces a decrease in signals.

The other reaction conditions, i.e. flow rate (0.3 - 1.8 ml/min) and mixing coil length (20 - 160 cm) were also optimized. As shown in Fig. 10, the highest signals were obtained at a flow rate of 0.6 ml/min. Higher than this flow rate, lower signals were found, because the complex formation between iron(III) and thiocyanate was reduced very much. The mixing coil length of 20 cm gave suitable response and was selected for further studies.

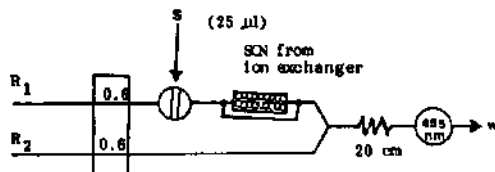


Fig.8: Dual channel FIA system for the determination of sulphide (method C) R1 (dionised water), R2, [Fe(III) solution]. Sulphide standards (25 μl) were injected in the line of ion-exchanger column (5 cm).

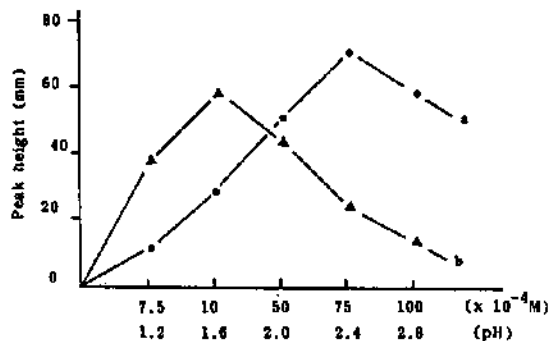


Fig. 9: a) Effect of Fe (III) solution concentration (M) and (b) its pH on the complex formation.

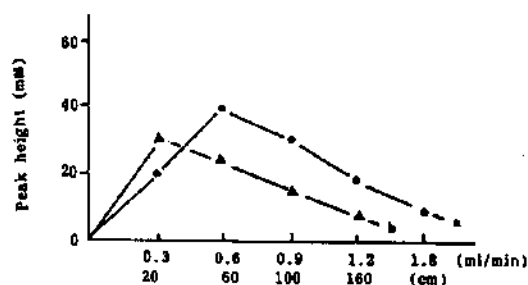


Fig. 10: a) Effect of flow rate and b) mixing coil length on the response of the detector.

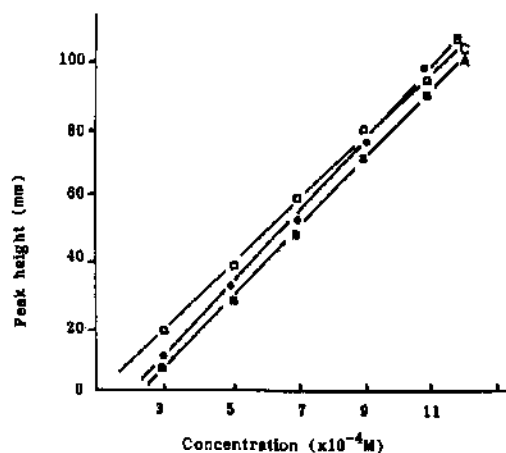


Fig. 11: Calibration graphs for sulphide by method A, B, and C.

The effect of ion-exchanger column length 3 - 7 cm (2.0 mm i.d) were tested. A column length of 5 cm gave the significant peak height. Increase in column length, caused some increase in dispersion

of the sample which resulted in slight decrease in peak height and time consumption. A column of ion-exchanger of 5 cm was selected for further studies.

Calibration Graph

Five standards of sulphide covering the range $3-11 \times 10^{-4}M$ were injected into the optimized system. Linear calibration graph was obtained as shown in Fig. 11. A distinct flow injection signal could be obtained with solution containing 0.5 mg/l sulphide, but below this range noise interfered with the signal measurement. The sampling rate was 45 samples/hr. The relative standard deviation was 0.4% for 10 measurements.

Effect of Diverse Ions

The effect of various anions on sulphide concentration was studied by addition method in all three established methods and the results obtained are summarized in the given Table 1.

Table 1: Effect of various anions sulphide concentration
Method A, Sulphide Standard $5 \times 10^{-4}M$, peak height = 95 mm Method B, peak height = 105 mm Method C, peak height = 103 mm

Anions	Concentration (M); Peak Height-mm		
	Method A (10 fold)	Method B (10 fold)	Method C (10 fold)
Acetate	ND	100	ND
Chloride	ND	115	135
Nitrate	ND	107	155
Oxalate	ND	103	ND
Phosphate	ND	ND	112
Sulphate	90	95	145
Sulphate	96	2.0	140
Thiosulphate	85	110	ND

Mean of three results (ND = Not determined)

As shown in table 1, the effect of various anions sulphide response is negligible on method A and B. However sulphite was a serious interferent in method B. In method C, these anions when injected into the carrier stream (Fig. 8) and by passed through the ion-exchange column did not give any response which means they do not form complex with iron (III). But on passage through the ion-exchange column they resulted in high response showing the displacement of thiocyanate by these ions from the column. For improving the selectivity of this method an interference suppressor column

(3 cm long 2.0 mm i.d) was incorporated into FIA manifold (Fig. 8) prior to the thiocyanate exchanger column. No response was obtained when sulphide was injected. This also resulted in precipitation inside the column and therefore the idea was dropped.

Conclusion

The first two established methods (A and B) are selective and sensitive and free from common interfering ions and therefore can successfully be applied to diverse samples in industry.

The method 'C' is very simple and sensitive. But is subjected to serious interferences from other ions. Therefore if this method is to be applied to real samples then ways have to be found to free it from interferences.

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