

FLOW-INJECTION SPECTROPHOTOMETRIC DETERMINATION OF SULPHIDE BY CATALYTIC REDUCTION OF TOLUIDINE BLUE

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ABSTRACT : Sulphide was determined spectrophotometrically at 628nm and pH 6.7 based on its catalytic reduction of toluidine blue in the presence of Se(IV) using a flow injection system. After optimization of the measuring conditions the calibration curve was found linear up to $25\mu\text{g mL}^{-1}$ and the detection limit was $0.3\mu\text{g mL}^{-1}$ (30 μL injections). The relative standard deviation for the determination of $10\mu\text{g mL}^{-1}$ sulphide was 1.2% ($n=14$). The injection rate was 30h^{-1} .

KEY WORDS : Sulphide, Toluidine Blue, Se(IV), Flow Injection, Spectrophotometry.

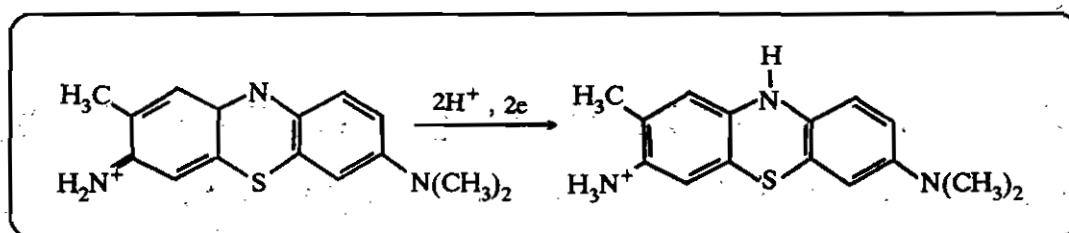
INTRODUCTION :

Because of the widespread industrial and biological effects, even at low concentration [1] of sulphide ion, there has been an increasing interest in the determination of this anion. Beside many different classical and spectrophotometric methods utilized [2-4], several direct, indirect

and catalytic methods for the determination of sulphide by flow injection analysis have also been described [5-8].

The well known reduction reaction of toluidine blue by sulphide ion, catalyzed by trace levels of selenium(IV), has been adopted as a

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selective and sensitive method for detection of selenium [9,10] and sulphide ions [11]:

The reaction can be easily monitored spectrophotometrically, since the reduced form of the dyestuff is colorless.

In this paper, a procedure for the rapid and selective determination of sulphide, involving a simple FIA technique, is described. The method is based on the catalytic reduction of toluidine blue by sulphide ion at pH 6.7 in the presence of constant Se(IV) traces.

EXPERIMENTAL :

Materials :

All chemicals used were of highest purity available and used without any further purification except for vacuum drying over P_2O_5 . Triply distilled water was used throughout.

Sulphide stock standard solution, $1000\mu\text{g mL}^{-1}$

Prepared by dissolving 0.7500g of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (Hopkin and Williams) in water and diluting to 100mL in a calibrated volumetric flask. The solution was prepared freshly and standardized [2]. The working solutions were prepared by appropriate dilution of the stock solution with water.

Toluidine blue stock solution, $500\mu\text{g mL}^{-1}$

Prepared by dissolving the dyestuff (Merck) in water.

Selenium(IV) stock solution, $1000\mu\text{g mL}^{-1}$

prepared by dissolving 0.1405g of SeO_2 (Merck) in water and diluting to 100mL in a calibrated volumetric flask. The solution was standardized iodometrically [2].

Apparatus :

For the spectrophotometric determination of sulphide, the flow injection manifold shown in Fig. 1 was used. The manifold tubing was a 0.5mm teflon tubing and the mixing tees were also made of teflon. Samples were injected using a rotary *Rheodyne* valve with a sample loop of $30\mu\text{L}$. A twelve - channel peristaltic pump (*Desaga*) was used for propelling the carrier and reagents. A *Bausch and Lomb UV-Vis Spectronic 70* equipped with a flow cell ($8\mu\text{L}$), connected to a *Perkin- Elmer R 100* chart recorder, was used to record the absorbance of toluidine blue at 628nm. The mixing coil was thermostated at 25°C .

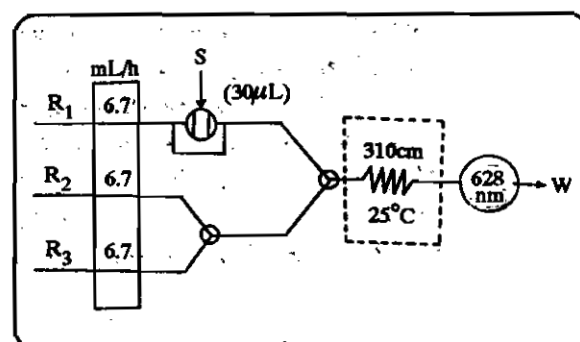


Fig. 1 : FIA manifold for the determination of sulphide.

R_1 , water; R_2 , toluidine blue and buffer solution;
 R_3 , Se(IV) solution.

Method :

Samples and standards were examined using the flow system shown in Fig.1 under the following optimized conditions: length of mixing coil = 310cm, flow rates of different streams = 6.7 mL h^{-1} , sample injection volume = $30\mu\text{L}$, Se(IV) concentration = $2\mu\text{g mL}^{-1}$ and toluidine blue concentration = $15\mu\text{g mL}^{-1}$ with 5% citrate buffer at pH 6.7.

RESULTS AND DISCUSSION :

We have previously observed that at neutral pH (pH=6.7, citrate buffer) toluidine blue undergoes a catalytic reduction reaction with sulphide ion in the presence of traces of Se(IV)[10,11]. It was found that, at constant concentration of Se(IV), the rate of reduction reaction (1) is proportional to the sulphide concentration. Since the reduced form of toluidine blue is colorless, the absorbance signal of the dyestuff at 628nm was found to have a linear decrease with the increased sulphide concentration.

Effect of Variables :

Various chemical reaction variables and flow injection variables were investigated in order to obtain the optimum conditions for the system. They were optimized by placing all variables constant and optimizing one at a time.

Our previous studies on the selenium - catalyzed reduction of toluidine blue with sulphide have shown that the optimum pH range for the reaction is 6.7-7.5 [10,11]. In this study, the influence of toluidine blue concentration, Se(IV) concentration and percentage of the citrate buffer (pH=6.7, 0.1M) in the dye solution on the reduction reaction were examined. The maximum decrease in the absorbance signal of toluidine blue was observed at $15\mu\text{g mL}^{-1}$ of the dyestuff, $2\mu\text{g mL}^{-1}$ of Se(IV) and 5% of buffer solution.

In FIA systems, the height of response peak depends on the residence time of the sample zone in the system, i.e., on the flow rate and the tube length. Fig. 2 shows the influence of flow rate and mixing coil length on the peak height. At a flow rate of 6.7 mL h^{-1} the best response was achieved; the lower flow rates gave higher peaks, but their reproducibility was unsuitable and the peaks broadened leading to lower sample throughput.

From Fig. 2, it can also be seen that there is a gradual increase in the response peak with increasing the length of the reaction coil from 90cm to 310cm, but thereafter no significant

change in the sensitivity was observed. A mixing coil length of 310cm was thus selected.

The effect of sample volume was also investigated in the range of 20 to $200\mu\text{L}$, to obtain the best overall response. A sample volume of $30\mu\text{L}$, gave the highest response.

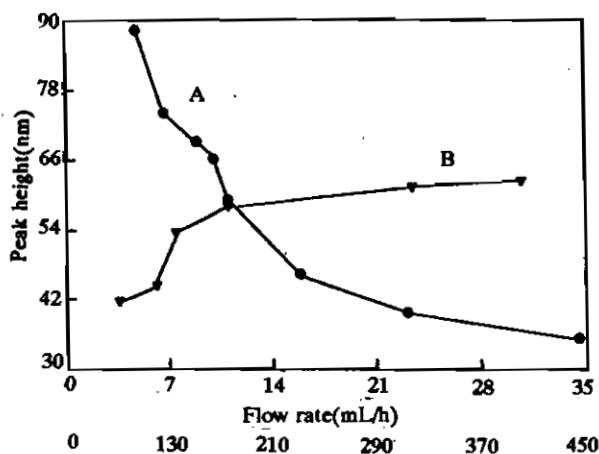


Fig. 2 : Effects of flow rate (A) and mixing coil length (B) on the peak height.

Conditions: toluidine blue, $15\mu\text{g mL}^{-1}$; pH=6.7, Se(IV), $3.0\mu\text{g mL}^{-1}$, sulphide, $20\mu\text{g mL}^{-1}$ mixing coil length, 310cm for curve A; flow rate, 11 mL h^{-1} for curve B.

Calibration :

Under the optimum conditions described above, in the concentration range of 0.5 to $25\mu\text{g mL}^{-1}$ of sulphide ion the following regression equation was obtained:

$$S = 3.702 + 3.203C$$

$$(r=0.9986)$$

Some typical peaks obtained for different concentrations of S^{2-} are shown in Fig. 3.

The detection limit ($3 \times \text{noise}$) was $0.3\mu\text{g mL}^{-1}$ and the sampling rate was 30 h^{-1} . The relative standard deviation of 14 replicate measurements is 1.2% for a $10\mu\text{g mL}^{-1}$ sulphide (Fig. 4).

Interference Studies :

Alkali and alkaline earth cations do not interfere the sulphide determination. The presence of cations such as Bi^{3+} , Ag^+ , Pb^{2+} and Pd^{2+} which can form insoluble precipitates with

sulphide ion would interfere its determination.

Many anions such as NO_3^- , PO_4^{3-} , HPO_4^{2-} , CH_3COO^- , HSO_4^- , NO_2^- , SO_4^{2-} , CO_3^{2-} , HCO_3^- , SCN^- , $\text{S}_2\text{O}_3^{2-}$, CN^- , OCN^- , halides, borate, citrate and EDTA had no considerable effect on

the determination of sulphide. However, sulphite ion was found to interfere the determination of sulphide seriously. The interfering effect of this anion was effectively removed using formaldehyde as masking agent [4].

CONCLUSIONS :

The method described provides a reliable means of determining trace amounts of sulphide. Its simplicity and precision are coupled with the high speed of FIA technique. The method should be applicable to the determination of sulphide in real samples, especially in natural waters [11].

ACKNOWLEDGMENT :

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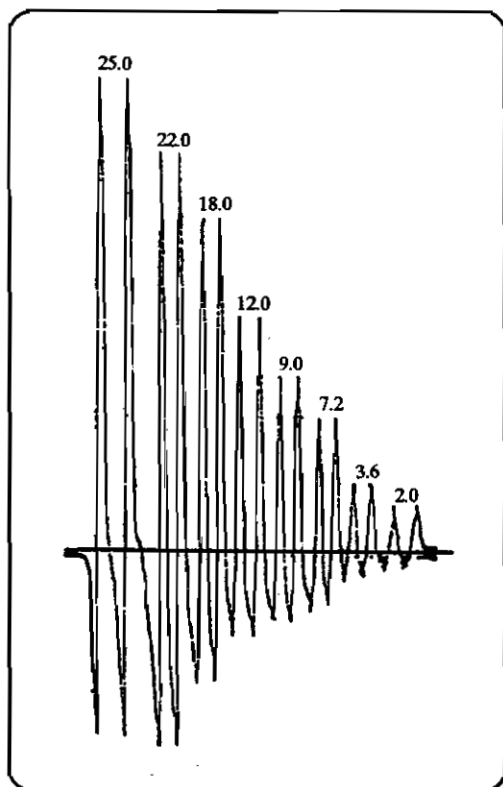


Fig. 3 : Peaks obtained for duplicate injections of various concentrations of sulphide. The numbers on the peaks show concentrations of sulphide in $\mu\text{g mL}^{-1}$.

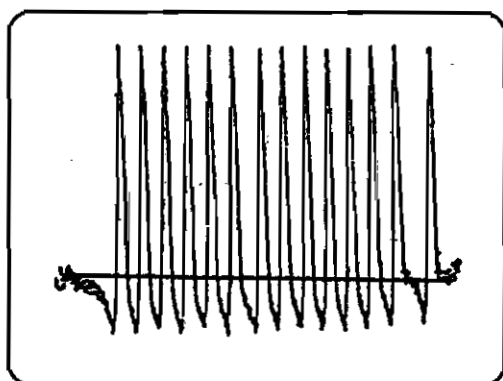


Fig. 4 : Peaks obtained for the replicate measurements of $10\mu\text{g mL}^{-1}$ sulphide.