214 Jour. Chem. Soc. Pak. Vol 20, No. 3, 1998

Spectrophotometric Determination of Sulphide Using Flow Injection Analysis

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(Received 25th October, 1997, revised 15th July, 1998)

Summary: A spectrophotometric flow injection procedure for the determination of sulphide is described. The reaction is based on the reduction of Fe(III) to Fe(II) by sulphide in acidic medium in the presence of 1,10 phenanthroline forming the orange-red complex $[(C_{12}H_8N_2)_3\ Fe]^{2+}$ measured at 510 nm. The detection limit was lower than 1×10^{-6} M with sampling rate of 50 h^{-1} having a relative standard deviation of 0.96% (n=10).

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 to aquatic life in concentrations well below 1 mgl^{-1} [1]. It attacks metal directly and indirectly causing serious corrosion of concrete sewers since it is oxidized biologically to sulphuric acid on the pipe wall.

Various spectrophotometric methods at present are available for the determination of small amounts of sulphide in water. These include the organic mercury compounds with sulphide in the presence of nitroprusside [2-4], methylene blue method [5] and the reduction of iron (III) in the presence of 1,10 phenanthroline [6,7] and others [8-10]. In the present study we describe a flow injection procedure for the determination of sulphide based on the reaction between sulphide ion and Fe(III) in acidic medium in the presence of 1,10 phenanthroline forming an orange-red complex measured at 510 nm.

Results and Discussion

In order to obtain a system with high precision, various experimental parameters were studied including reagents concentration, flow rate and mixing coil length (Table-1). These parameters were optimized by placing all variables constant and optimizing each at one time.

Table-1: Effect of various parameters on the determination of sulphide

Iron (III) (M)	0.001	0.005	0.01	0.05	0.1
Absorbance*	0.025	0.047	0.056	0.047	0.033
1,10 phenanthroline (%)	0.01	0.05	0.1	0.15	0.2
Absorbance*	0.01	0.02	0.04	0.03	0.02
Mixing coil length (cm)	50	100	150	200	250
Absorbance*	0.05	0.07	0.06	0.05	0.04

*Mean of three readings.

The effect of Fe(III) was investigated over the range (0.001-0.1 M) prepared in acetic acid (0.01 M) optimized (results not shown). The absorbance increased with increasing concentration of Fe(III) upto 0.01 M, further increase resulted in decrease of absorbance due to the saturation of reagents with respect to Fe(III). An optimum concentration of 0.01M was used subsequently.

To investigate the optimum concentration of 1,10 phenanthroline for complex formation, different concentrations of the compound covering the range of 0.01 - 0.2% were studied. The absorbance increased with increasing the amount upto 0.1% (w/v). Above 0.1% the absorbance decreased due to the saturation of reagents with respect to 1,10 phenanthroline. A concentration of 0.1% was selected for further studies.

The effect of other parameters like flow rate and mixing coil length were also investigated. The effect of flow rate for carrier stream (Fe(III)) and reagent stream (1,10 phenanthroline) were studied over the range of 0.3-2.0 ml min^{-1}. A flow rate of 0.7 ml min^{-1} for sample carrier stream and 1.0 ml

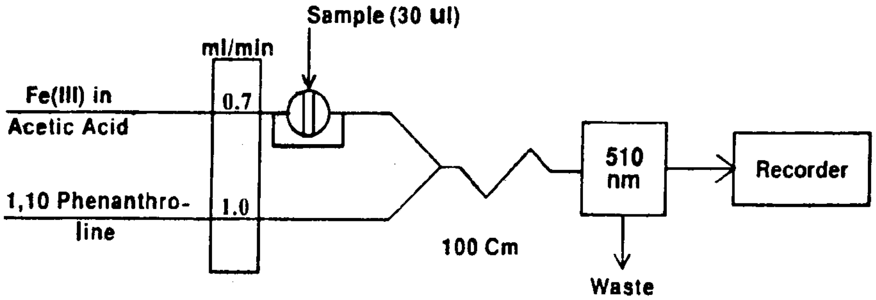

Fig. 1: Fl-spectrophotometric manifold for the determination of sulphide.

min^{-1} for reagent carrier stream gave maximum response. Further increase in flow rate decreased the absorbance due to rapid sample dispersion in the reaction coil. Therefore a flow rate of 0.7 ml min^{-1} for carrier stream and a flow rate of 1.0 ml min^{-1} for reagent stream were selected for further experimental studies. The effect of coil length on absorbance was investigated over the range of 50 - 250 cm. The absorbance increased with increasing coil length from 50 - 100 cm and decreased above 100 cm due to the dispersion of sample at longer residence time. A coil length of 100 cm was used subsequently.

Calibration data

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 as shown in Fig. 2 was linear over the range 2-10 x 10^{-5} M, with a correlation coefficient of 0.9995 (n=5) and a regression equation of y=0.0094 x-0.006 [y=absorbance; x=concentration (M)]. The limit of detection (2 x background) was lower than 1 x 10^{-6} M and the sampling rate was 50 h^{-1}. The relative standard deviation was 0.96% (n=10) of 1 x 10^{-4} M sulphide.

Effect of diverse ions

A serious drawback of the spectrophotometric methods for the trace determination of metal/nonmetals is the interferences by non-analyte present in sample. Therefore the effect of diverse ions on sulphide determination was studied. The results obtained are summarized in Table-2. Thiosulphate was found to interfere slightly while the rest tested did not show any considerable interference. The method developed therefore is comparatively selective.

Table-2: Effect of diverse ions (1 x 10^{-3} M) on the determination of sulphide (1x10^{-4} M).

Ion tested	Added as	Peak absorbance*
Sulphide	sodium	0.10
Thiosulphate	sodium	0.07
Hydrogen phosphate	potassium	0.01
Chloride	magnesium	0.00
Nitrate	potassium	0.003
EDTA	sodium	0.01
Fluoride	sodium	0.00
Iodide	potassium	0.001
Urea	--	0.01

*Mean of three readings.

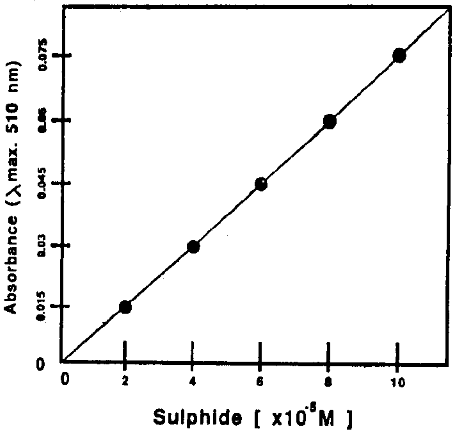

Fig. 2: Calibration graph for sulphide determination by Fl-spectrophotometry

Experimental

Materials and methods

All reagents used were of analytical grade (Merck, BDH) and solutions were prepared in distilled/deionized water.

Iron (III) solution (0.1 M) was prepared by dissolving 2.7 g of iron (III) chloride hexahydrate in 100 ml of water containing 0.01 M acetic acid.

1,10 phenanthroline solution (0.2%) was prepared by dissolving 0.2 g of the monohydrate compound in hot water (70°C) and after cooling, the solution was made upto a volume of 100 ml with water.

Sulphide stock solution (0.1 M) was prepared fresh whenever required by dissolving an appropriate amount of $Na_2S.9H_2O$ in 100 ml of water. The surface of crystals was initially rinsed with water and washings were discarded. The sulphide contents was determined iodimetrically and various standards solutions were prepared by serial dilution with water.

Instrumentation

The FIA manifold shown in Fig. 1, samples were injected using a rotary value (Rheodyne 5020) with a sampling loop of 30 μl. A peristaltic pump (Ismetic Reglo 100) was used for propelling the carrier (0.7 ml min^{-1}). PTFE tubing (0.8 mm i.d.) was used throughout the manifold. The absorbance of orange-red complex was monitored at 510 nm using a spectrophotometer (Hitachi U-1100) equipped with a flow through cell (30 μl). Spectrophotometer was connected to a chart recorder (Kipp and Zonen BD 40).

Conclusions

The FIA-spectrophotometric method established shows a simple, rapid and inexpensive mean of determining sulphide at trace levels. The effect of diverse ions on the analytical response of interest is negligible and the method can therefore be applied to sulphide in environmental and industrial samples.

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