

Determination of Sulphide in Sediments and Sewerage Water by Indirect Conductometry

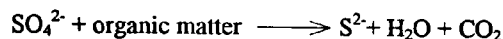
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Summary: A conductometric method has been developed for the determination of sulphide in sediments and sewerage water samples. The method is based on the separation of sulphide as hydrogen sulphide by treating the sample with sulphuric acid. The produced hydrogen sulphide was swept to an absorption solution of copper sulphate with the help of a nitrogen stream. The increase in the conductivity of absorption solution was measured and plotted against sulphide concentration to obtain the calibration. The effects of concerned parameters were checked and the method was applied to the real samples of sewerage water and sediments.

Introduction

In the absence of sufficient quantities of oxygen, usually in sewers, sulphates serve as a source of oxygen for biochemical oxidation produced by anaerobic bacteria. Under anaerobic conditions, the sulphate ion is reduced to sulphide ion [1].



The sulphide ion produced establishes an equilibrium with hydrogen ion to form hydrogen sulphide.



The concentration of S^{2-} , HS^- and H_2S highly depend upon the pH of the system. At pH values of 8 and above most of the reduced sulphur exists in solution as HS^- and S^{2-} ions and the amount of H_2S is so small that its partial pressure is insignificant and odour problems do not occur [2]. At pH levels below 8, the equilibrium shifts rapidly towards the formation of unionized H_2S and is about 80% complete at pH 7. Under such conditions the partial pressure of H_2S becomes great enough to cause serious odour and pollution problems whenever sulphate reduction yields a significant amount of sulphide ions [3].

At low concentration hydrogen sulphide causes irritation of eyes and respiratory tract,

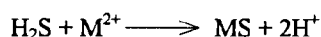
headache, dizziness and if exposure is prolonged bronchitis may result. Higher concentrations of the gas can paralyse the nervous system, respiratory system and digestive system. With repeated exposures to low concentrations conjunctivitis, photophobia, corneal bullae, tearing, pain and blurred vision are the common findings [4,5].

Besides its toxicity to human life, hydrogen sulphide is considered responsible for corrosion in sewer systems. Bacteria of the genus *Thiobacillus* are capable for sulphide oxidation to sulphuric acid, at pH as low as 2, this is the acid which thought to be responsible for corrosion problems [6].

A number of spectrophotometric methods [7-9] have been developed for sulphide determination but little attention has been paid towards its estimation by conductometry which is relatively more simple, inexpensive and available technique in common laboratories. Probably the reason is that in spite of the high sensitivity of the technique, direct conductometric measurements suffer from a lack of selectivity because every charged species, present in the matrix, contribute to the total conductivity of the sample solution.

In present work a method is described in which the conductivity is incorporated by isolating the sulphide as hydrogen sulphide which has been absorbed in a solution to form an insoluble metal sulphide:

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(M = Cu, Ni, Pb, Zn and Cd)

The increase in conductivity of absorption solution, mainly due to H^+ ions was measured and plotted against sulphide content of the sample.

Results and Discussion

Absorption of hydrogen sulphide

Hydrogen sulphide produced in the sample tube was swept by a nitrogen stream to the solution of a metal salt capable of forming insoluble sulphide. The soluble salt, like nitrates of silver(I), lead(II), and cadmium(II) and sulphates of copper(II), nickel(II) and zinc(II) were used for this purpose. The relative increase in conductance occurred in equimolar solutions of different metal salts, by using the same amounts of sulphide, is shown in Fig. 2. The maximum increase in conductance was observed in the case of copper sulphate. Whereas increase in conductance using zinc and nickel solutions was almost half than that found in copper(II) salt. Silver

nitrate as the absorbing solution gave a calibration with very high intercept and very low slope. Lead and cadmium nitrates yielded significantly curved calibrations with inadequate linearity. As copper sulphate gave a linear calibration line passing through the origin and with an ideal slope, therefore the absorbing solution of this salt was used throughout this work.

Although all the metals used form sparingly soluble sulphides but the difference in calibrations obtained was probably due to the differences in the characteristics of the metal salts, and the solubility product of respective metal sulphides. To check the effect of the concentration of absorbing solution three solutions of copper sulphate, $5 \times 10^{-2}\text{M}$, $1 \times 10^{-3}\text{M}$, $1 \times 10^{-4}\text{M}$ were used. No significant difference in the increase in conductance was found for the same amount of sulphide. The initial conductance values of all the three solutions were different and the best results were obtained with $5 \times 10^{-2}\text{M}$ solution. Effect of the volume of absorbing solution was checked by taking 10-50mL of $5 \times 10^{-2}\text{M}$ copper sulphate solution. The maximum increase in conductance was

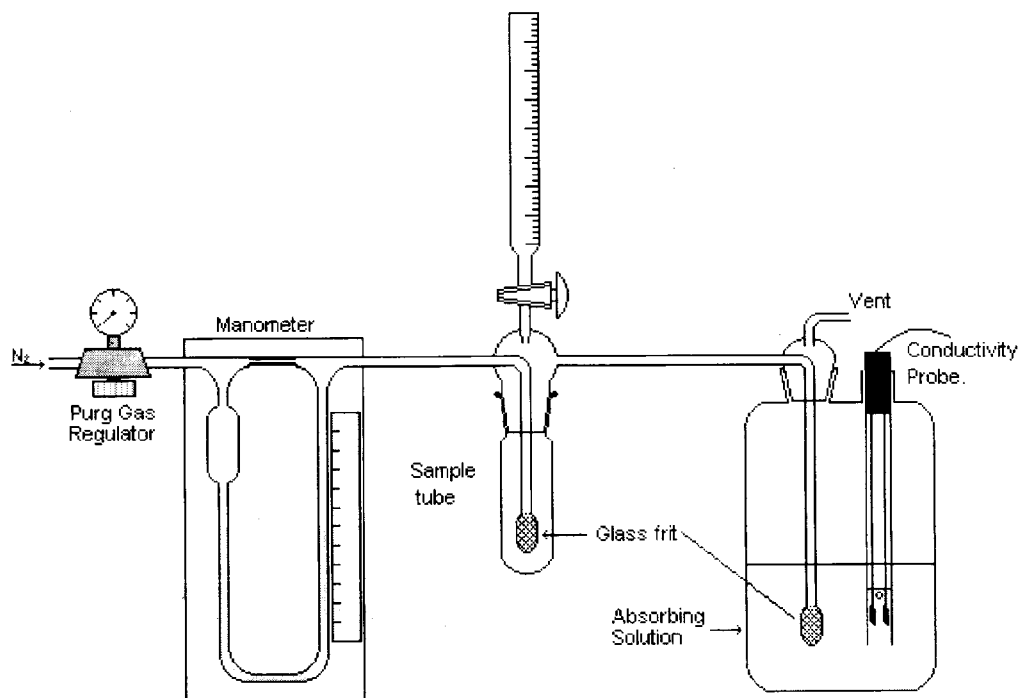


Fig. 1: Apparatus assembly used for sulphide determination.

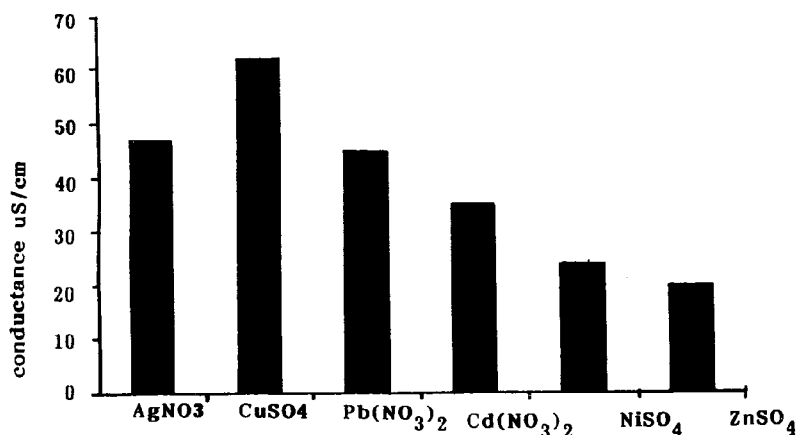


Fig. 2: Relative increase in conductance using equimolar solutions of different metal salts.

observed when 25-30mL solution was taken (Fig. 3). Low value of conductance for lesser volumes was probably due to the fact that H₂S could not be completely absorbed by the solution whereas a slight decrease at higher volumes is because of dilution.

Although pH has a significant role in the dissociation of H₂S but as the increase in conductance in solution was mainly due to hydrogen ions therefore no attempt was made to alter the pH by adding any acid or base to the absorbing solution.

Calibration and precision

Fig. 4 shows the calibration obtained when H₂S from 0.5-2.5μM of sulphide was absorbed in 5×10⁻²M solution of copper sulphate and increase in conductance of the solution was plotted against sulphide concentration. It was almost linear and passing through the origin. Precision of the method was evaluated by calculating the standard deviation for the sulphide contents obtained when seven aliquots of the same sewerage water sample were analyzed by the described procedure. The value of standard deviation obtained was 0.0064 μM.

Effect of nitrogen flow rate and temperature

Nitrogen was used to sweep the produced H₂S into absorbing solution. Effect of nitrogen flow rate was checked on the final value of conductance. No significant difference in the conductance was found when nitrogen was flown from 1-21/min. However a

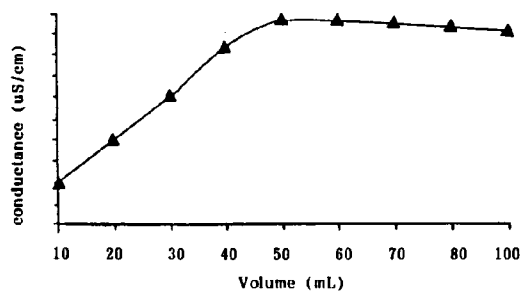


Fig. 3: Effect of volume of Copper(II) sulfate solution.

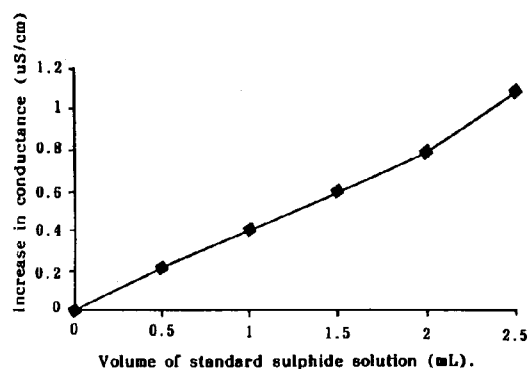


Fig. 4: Calibration curve for sulphides.

considerable decrease in the conductance was observed when the flow rate was exceeded from 21/min. This decrease was probably due to the incomplete absorption of H₂S at higher flow rates.

hence nitrogen was passed at 21/min through out this work.

To check the effect of temperature, H₂S was generated at elevated temperatures (40-80°C) of the sample and passed through the absorbing solution but no considerable difference has been found in the conductance values than that obtained at room temperature.

Effect of acid strength and volume

Sulphuric acid was used to liberate the H₂S from sulphide samples. The effect of sulphuric acid strength was checked by using the acid aliquots of different strengths. Almost equal values of conductance were obtained when 1 mL of 2-6M sulphuric acid was used to yield H₂S from sulphide samples up to 2 mL. However when more than 2 mL acid was used to liberate H₂S from relatively larger volumes of sulphide solution the final conductance was significantly decreased. This was probably due to the trapping of H₂S in larger volume of acid and the sample in H₂S generation tube.

Effect of interfering ions

Effect of a number of common anions and cations have been checked by analysing the sulphide samples in presence of equimolar quantities of these ions. As shown in Table-1, none of the cation except lead showed any appreciable effect on the sulphide determination. Lead gave noticeably lower results probably due to the formation of insoluble lead sulphide. Other cations like sodium, calcium, zinc, magnesium, iron, aluminum, nickel, cobalt and potassium did not show any considerable error in sulphide results.

Among the anions, however, chloride enhanced the conductance significantly, which was probably due to the volatile HCl formed on addition of sulphuric acid and swept along H₂S to absorption solution. Other common anions such as sulphate, nitrate, phosphate, carbonate, acetate, iodide, bicarbonate, thiocyanate, and bromide did not add any appreciable error in results.

Water and sediment samples

Water and sediment samples were collected from local sewerage system and analysed by the described as well by Ethylene Blue Method. The results obtained by both methods are shown in Table-2. As shown by the Table, the results of all the six water samples obtained by both methods are well in agreement with each other whereas the results of two of the sediment samples, obtained by both the methods were significantly different. This difference may be due to the fact that these samples were not completely homogenized.

Experimental

Reagents and equipment

All the chemicals used in this work were of laboratory grade. The doubly distilled conductivity water was used. The conductivity measurements were made on a Syntax Conductivity Meter, Model Sc-16A equipped with standard conductivity cell.

Standard solutions

One gram of AnalaR Grade sodium sulphide (rinsed with absolute ethanol and dried) was dissolved in 100 mL water and the solution was standardized iodometrically. A standard sulphide solution, 1x10⁻³M, was prepared by dilution.

Table-1: Effect of diverse ions on sulphide determination.

Anion	Added as	Concentration	% Error.	Cation	Added as.	Concentration	% Error
Cl ⁻	Sodium	Same as S ⁻	+5.1	Na ⁺	Sulfate	100 folds	+0.2
Br ⁻	Potassium	Same as S ⁻	+2.5	K ⁺	Sulfate	100 folds	+0.0
SO ₄ ⁻	Sodium	Same as S ⁻	-2.0	Ca ⁺⁺	Carbonate	100 folds	+1.5
NO ₂ ⁻	Potassium	Same as S ⁻	-1.06	Mg ⁺⁺	Sulfate	100 folds	+1.0
NO ₃ ⁻	Sodium	100 folds	-2.2	Pb ⁺	Nitrate	Same as S ⁻	-7.0
HCO ₃	Sodium	100 folds	-1.6	Fe ⁺⁺⁺	Sulfate	10 folds	-2.0
CH ₃ COO ⁻	Sodium	100 folds	-0.5	Al ⁺⁺⁺	Sulfate	10 folds	-2.2
I ⁻	Potassium	Same as S ⁻	+2.0	Ni ⁺⁺	Sulfate	100 folds	-1.5
SCN ⁻	Potassium	10 folds	+1.2	Co ⁺⁺	Sulfate	100 folds	-1.2
PO ₄ ⁻⁻⁻	Sodium	10 folds	+1.5	Zn ⁺⁺	Sulfate	100 folds	-0.5

Table-2: Sulphide found in sewerage water and sediment samples by described and reference methods.

Sample	Sulphide found ($\mu\text{g/gm}$) by	
	Described method	Ethylene blue method
Sewerage water		
A.	48.0	50.2
B.	62.2	64.0
C.	42.8	43.6
D.	50.2	50.0
E.	58.6	60.2
F.	52.4	50.2
Sediments		
1.	520	525
2.	425	490
3.	550	565
4.	510	570
5.	505	500
6.	325	330

Copper(II) sulphate $5 \times 10^{-2} \text{M}$ solution was prepared by dissolving 0.50 g of the salt in one liter of water.

Apparatus assembly

A schematic diagram of the overall assembly is shown in Fig. 1. A calibrated manometer was used to monitor the gas flow rate. The hydrogen sulphide generator consists of an acid reservoir and a sample tube. The sample tubes were 10x2 cm Pyrex tubes with quickfit sockets. On addition of a known volume of acid from the reservoir, the H_2S produced was swept by a nitrogen stream to an absorption solution taken in a gas wash bottle fitted with a conductance probe.

Calibration

Set up the apparatus and make the gas connections between nitrogen cylinder, flow meter, sample tube and gas wash bottle. Fit a clean empty tube on the bubbler and flush the whole set-up with nitrogen. Adjust a constant flow of nitrogen gas through the assembly. Fill the reservoir with 2M sulphuric acid. Transfer 0.2 to 1 mL aliquots of $1 \times 10^{-3} \text{M}$ sulphide solution into a sample tube by an Agla Syringe. Fit the sulphide containing tube to the bubbler. After measuring the initial conductance of $5 \times 10^{-2} \text{M}$ copper sulphate, take 25 mL of this solution in the gas wash bottle. Run 2mL of sulphuric acid from the reservoir into the sulphide sample. The

carrier gas should constantly pass through the assembly and bubble from the gas wash bottle. Run the gas for 2 minutes and then replace the sample tube with an empty tube on the bubbler and measure the conductance of the solution in the gas wash bottle. Plot the increase in conductance against the sulphide content and prepare the calibration.

Sediment and water samples

Six water samples collected from different sewerage systems were filtered to separate the suspended solids and analysed by the described method as well as by a reference method [10]. Sediment samples, collected from sewerage, were dried in an oven at 120°C for four hours and then pulverized to get a homogenous powder. A known weight of this powder (0.2-0.5g) alongwith 2 mL water was taken in the sample tube, and analysed for sulphide content by the described procedure as well as by Ethylene Blue reference method [10].

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