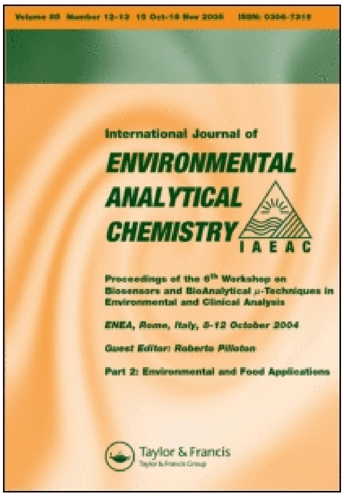

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Punta, A. , Barragán, F. J. , Ternero, M. and Guiraum, A.(1991) 'Determination of Sulphide in Sewage Effluents Using a New Spectrophotometric Method', International Journal of Environmental Analytical Chemistry, 43: 2, 91 — 101

To link to this Article: DOI: 10.1080/03067319108026969

URL: http://dx.doi.org/10.1080/03067319108026969

Intern. J. Environ. Anal. Chem., Vol. 43, pp. 91–101
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DETERMINATION OF SULPHIDE IN SEWAGE EFFLUENTS USING A NEW SPECTROPHOTOMETRIC METHOD

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(*Received 23 November 1989; in final form 10 June 1990*)

A suitable indirect spectrophotometric method for the determination of sulphide in water, based on the reduction of 1,2-naphthoquinone-4-sulphonate (NS) has been developed. The excess of NS is spectrophotometrically determined based on the red colour produced in its reaction with sulphanilic acid at pH 4.0–6.5. Maximum colour intensity is obtained after 40 min and the apparent molar absorptivity at 470 mm is 3.5×10^3 l.mol^{-1}.cm^{-1}. The sulphide concentrations can be calculated by the difference in absorption of blanks and samples.

The proposed method is performed at pH 5.2 in the presence of EDTA in order to enable dissolution of sulphide preserved as ZnS in the samples. The method has a range of determination of 0.8 to 8.0 μg.ml^{-1} of sulphide (variation coefficient = 1.2%, molar absorptivity coefficient = 2.6×10^3 l.mol^{-1}.cm^{-1} at 470 nm) and it is tolerant to a 150-fold excess of cyanide ion. A complementary procedure with a previous distillation step of hydrogen sulphide is described for water samples with suspended material, with natural colour or with low contents in sulphide. The methods were applied to determine sulphide in waste waters. The results were comparable with those obtained using the methylene blue method, which seems to be less selective and accurate but more sensitive than the present method.

KEY WORDS: Sulphide determination, water analysis, spectrophotometry, 1,2-naphthoquinone-4-sulphonate, sulphanilic acid.

INTRODUCTION

Sulphide determination is important in water quality control and many procedures for the determination of microamounts of sulphide in waters are found in the literature. *In situ* measurements of sulphide activity are possible with ion-selective electrodes,[1,2] which involve non-elaborate sample handling and easy calibration. However, determination of total sulphide can be accomplished only in solutions of well-known ionic strength and sulphide electrodes often show memory effects and have a slow response. The determinaton of sulphide by NP polarography[3,4] shows serious interferences, specially from heavy metals and organic materials. Best results are obtained by using cathodic stripping voltammetry,[5,6] which allows sulphide to be pre-concentrated and, hence, yields better selectivity and sensitivity. Fluorimetric methods based on the quenching of a fluorescent chelate[7,8] or an

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increase of fluorescence intensity of a non-fluorescent chelate[9,10] due to the action of sulphide ion on the metal and based on condensation of sulphide to give a fluorescent compound,[11] have also been reported.

The microscale determination of sulphide is most often carried out by using the methylene blue method which is accepted as standard procedure.[12] This spectrophotometric method has numerous modifications.[13–18] Sulphide ions have also been determined spectrophotometrically in homogeneous medium by the use of sodium nitroprusiate,[19] ammonium molybdate,[20] iodine-azide[21] and via extraction procedures using copper chelates.[22,23] Recently, the 1,2-naphthoquinone-4-sulphonic acid (NS) reaction for sulphanilic acid and sulphonamides was applied to their spectrophotometric determination in pharmaceuticals.[24] In this previous study, the nature of the reaction product NS-sulphanilic acid was well established and it was observed that sulphide reacts with NS, diminishing the characteristic red colour produced in its reaction with sulphanilic acid, since sulphide reduces the quinone derivative NS. In the present work, we aimed at establishing a spectrophotometric method for sulphide based on these reactions.

EXPERIMENTAL

Apparatus

Spectrophotometer A Perkin–Elmer 554 UV-visible spectrophotometer with 1.0-cm silica cells was used.

pH meter A Beckman 70 pH meter with glass-calomel electrodes was used for pH measurements.

Distillation apparatus A standard distillation apparatus[25] equipped with a 250-ml distillation flask was used. This flask is fitted with a dropping funnel and a gas inlet so that nitrogen as inert gas can be bubbled through the solution. The receiver used was a 100-ml volumetric flask.

Reagents

Sulphide standard solution Prepare an approx. 100 mg.l^{-1} sulphide solution by dissolving 0.75 g of sodium sulphide nonahydrate in 1 litre of water. Renew and standardize it every day by the iodometric method. The solutions were used within 6 h.

1,2-Naphthoquinone-4-sulphonic acid solution Prepare a 3.26×10^{-3} M solution by dissolving 0.09 g of the potassium salt in 100 ml of water. Since the product is susceptible to photochemical decomposition, the solutions must be stored in an amber-coloured bottle and daily prepared.

Sulphanilic acid solution Prepare a 2.14×10^{-2} M solution by dissolving 0.3706 g of the reagent in 100 ml of water.

Acetic acid–potassium acetate buffer solution Prepare a pH 5.2 buffer solution (0.1 M total concentration) by dissolving 6 ml of glacial acetic acid and 3.5 g of potassium hydroxide in 1 litre of water.

Zinc acetate solution Prepare an approx. 0.1 M solution by dissolving 22 g of zinc acetate dihydrate in 1 litre of water. Dilute this stock solution as appropriate to produce an 0.01 M working solution.

Ethylenediamine tetraacetic acid solution Prepare an approx. 0.1 M solution by dissolving 40 g of disodium dihydrate salt in 1 litre of water.

Potassium chlorate solution Prepare an approx. 0.5 M solution by dissolving 61 g of salt in 1 litre of water.

Phosphoric acid solution Use an 85% (sp. grav., 1.71) concentrated phosphoric acid solution.

Nitrogen purifying solution Dissolve 5 g of mercury(II) chloride in 100 ml of 2% (w/v) potassium permanganate solution.

The reagents for the *methylene blue reference method* used for evaluating the performance of the proposed method were prepared as described in "Standard Methods".[12]

All reagents and solvents were of analytical-reagent grade. Distilled and deionised water was used.

Methods

Principle of the method NS is a quinone derivative and undergoes rapid reduction with sulphide ion to a stable product (reduced-NS). Reduced-NS does not react with sulphanilic acid to form a red product as NS does. So, when to a solution of sulphide ion a NS solution and, next, a solution of sulphanilic acid are added, a decrease of the red coloration compared with that of a blank sample without sulphide is observed. Decoloration is proportional to the amount of sulphide, and thus, on this basis, a method for the spectrophotometric determination of sulphide is proposed below.

Determination of sulphide in water Preserve the sample by putting 2 ml of 0.1 M zinc acetate solution into a 1000-ml bottle, filling-up with the sample and stoppering. Total sulphide was determined spectrophotometrically either by a direct method, or by distilling from acidic media as hydrogen sulphide. The latter procedure is recommended when samples show coloration or are not entirely free from suspended solids, or to concentrate the sulphide into a smaller volume for greater analytical sensitivity.

A) *Direct determination* Depending on the content of sulphide ions, transfer an accurate volume of shaken sample (up to 50 ml) containing 80–800 μg of sulphide, to a 100-ml volumetric flask wrapped with aluminium foil, and then add 2 ml of 0.5 M chlorate solution. After mixing, add 10 ml of pH 5.2 buffer solution, 8 ml of 3.26×10^{-3} M NS solution and 10 ml of 0.1 M EDTA solution. Mix and allow the flask to stand for 15 min, and then add 10 ml of 2.14×10^{-2} M sulphanilic acid solution and dilute to the mark with water. Prepare a blank solution similarly without sulphide. Measure the absorbance of both solutions at 470 nm against water after 40 min. Calculate the difference of the absorbance values between sample and blank. Prepare a calibration graph by using standard solutions treated in the same way.

B) *Determination with distillation* Depending on the content of sulphide ions, add up to 200 ml of the sample containing 80–800 μg of sulphide into a 250-ml distillation flask (for lower contents add up to 400 ml into a 500-ml distillation flask). Introduce 10 ml of pH 5.2 buffer solution, 2.5 ml of 0.01 M zinc acetate solution and 8 ml of distilled water into the 100-ml receiver volumetric flask. Heat to boiling under a moderate flow of nitrogen (2 ml.min^{-1}) which has passed a washing bottle with nitrogen-purifying solution. When water is already distilling over into the receiver, add 5 ml of phosphoric acid solution to the distillation flask through the dropping funnel. After 15 min, when the volume of liquid in the receiver is about 70 ml, cease distillation. Remove the volumetric flask and inlet tube from the apparatus. Wrap the volumetric flask with aluminium foil and follow the above procedure. Prepare the calibration graph by using standard solutions of sulphide treated in the same way.

RESULTS AND DISCUSSION

Reaction of NS with Sulphanilic Acid

NS reacts with sulphanilic acid at room temperature in aqueous acidic medium to form a red colour. All variables leading to maximum colour intensity and stability were optimized. The red product obtained under optimum conditions (pH 4.0–6.5, ≥6-fold molar excess of sulphanilic acid to NS and ≥40 min of reaction time to reach equilibrium) exhibits an absorption maximum at 470 nm ($\varepsilon_{max} = 3.5 \times 10^3$ l.mol^{-1}.cm^{-1}). Neither sulphanilic acid nor NS themselves absorb appreciably under the same conditions. The colour formation is not affected by the temperature in the range 20–70 °C or by the ionic strength of the medium. The colour remains stable at least 24 h. The action of sulphide on the NS/sulphanilic coloured system is illustrated in Figure 1.

Reaction of NS with Sulphide

NS solutions must be protected from light to prevent decomposition. Sulphide as well as other reducing agents reduce NS in the absence of light. Reduction of NS by sulphide is rapid and is complete in 15 min, leading to a stable reduced-NS product. Moreover, according to the study of the spectra of NS in the presence of

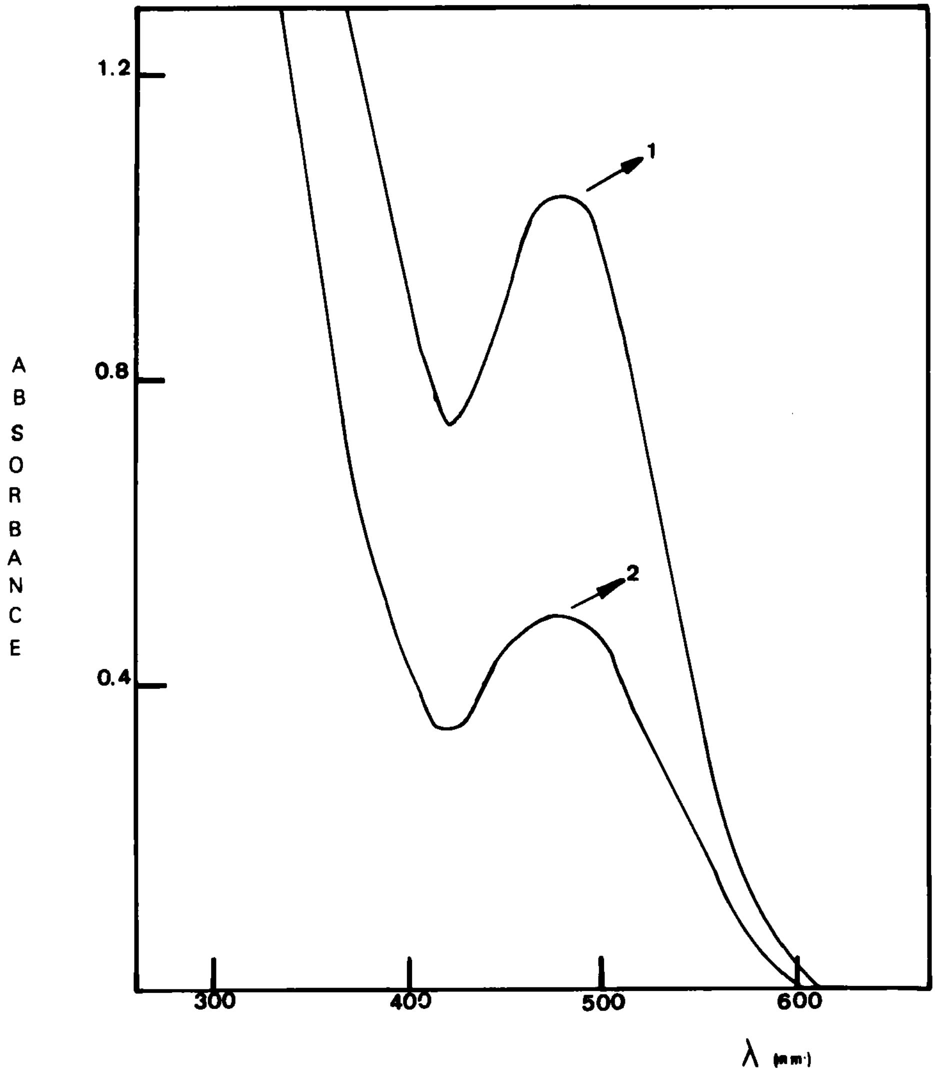

Figure 1 Spectra of the condensation product of 2.7 × 10^{-4} M NS with 2.2 × 10^{-3} M sulphanilic acid at pH 5.2 (1); the same solution in the presence of 2.7 × 10^{-4} M sulphide (2).

increasing amounts of sulphide, the decay of the absorption of the NS band with its maximum at 370 nm is proportional to the sulphide concentration (Figure 2). Reduced-NS does not affect the coloured reaction of remaining unreacted-NS with sulphanilic acid.

Spectrophotometric Determination of Sulphide

Sulphide can be determined by indirect spectrophotometry on the basis of the

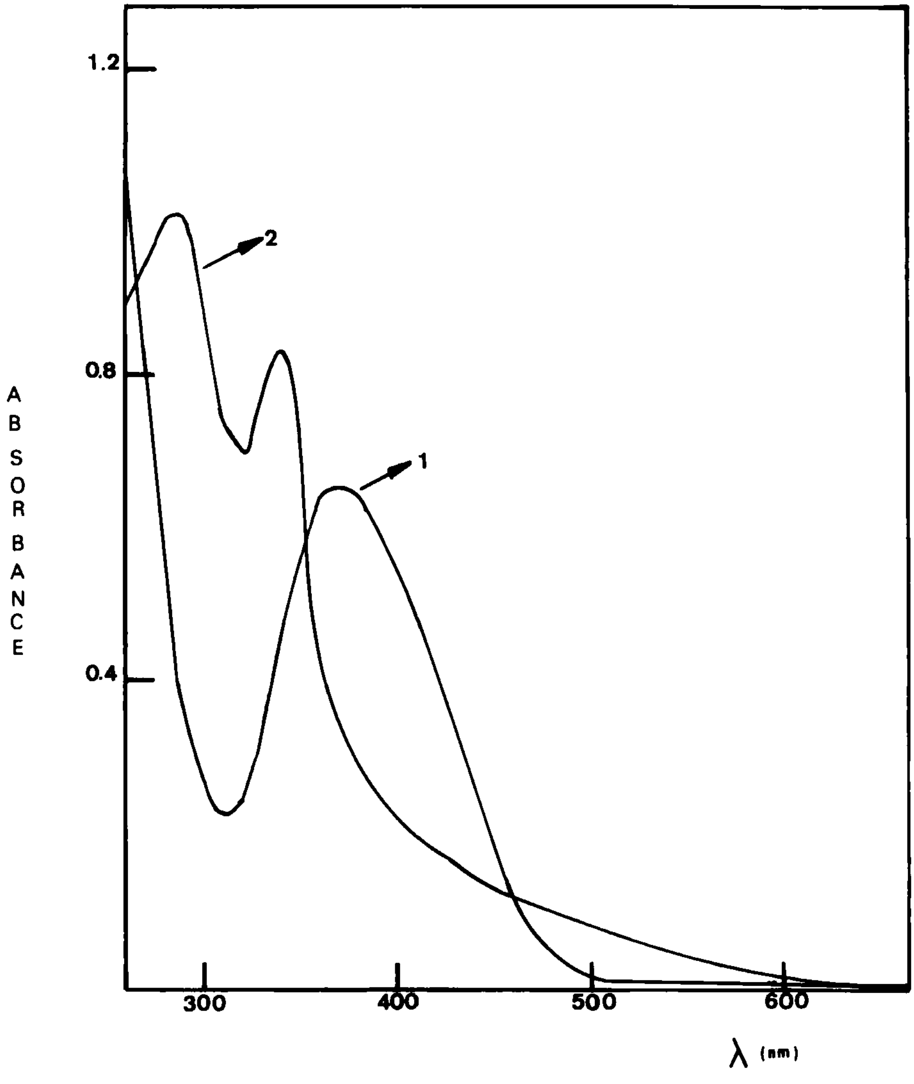

Figure 2 UV-visible spectra of 2.7×10^{-4} M NS at pH 5.2: (1) reagent alone, and (2) with an equal molar amount of sulphide.

above reactions. The sample with sulphide is treated with NS at pH 5.2 and, then, the unreacted-NS is condensed with sulphanilic acid to give the corresponding coloured derivative measurable at 470 nm.

The optimisation of variables influencing the sulphide/NS/sulphanilic acid system were studied again, the results being the same as those obtained previously for the reaction of NS and sulphanilic acid without sulphide present.

Based on the experimental work, a direct method and a distillation method are proposed for the spectrophotometric determination of sulphide.

Table 1 Recovery of sulphide in the presence of zinc acetate and/or EDTA[a]

Substance added ($\mu g.ml^{-1}$)		*Sulphide recovered* (%)
Zinc(II)	*EDTA*	
4.0	—	83.9
0.5	—	83.9
0.2	—	99.6
—	8.000	108.7
—	6.000	106.0
—	4.000	103.7
20.0	4.000	80.5
18.0	4.000	90.8
13.0	4.000	100.3

[a] Amount of sulphide taken: 86.0 μg/100 ml of sample.

Fixation of sulphide and use of EDTA as masking agent In order to establish the suitability of zinc acetate as reagent for the fixation of sulphide ion in water or for the collection of hydrogen sulphide in the distillation method, a preliminary interferences study was carried out in the presence of this substance. Besides, EDTA was considered as a possible agent to increase the zinc sulphide solubility, enabling its dissolution at the working pH of 5.2, and likewise to act as masking reagent for other cations which also form insoluble sulphides. EDTA is tolerable in the sulphide determination at a calculated level of a 4600-fold excess. The joint effect of these two substances was also investigated. The results of these studies for the determination of 86 μg of sulphide are shown in Table 1. From these results it is concluded that zinc acetate can be used at levels fixed in the procedure as preservant agent (2 ml of 0.1 M solution per litre of sample) and as adequate collector of hydrogen sulphide (2 ml) of 0.01 M solution per 100 ml of final volume), and that EDTA also works well in the proportion given in the procedure.

Direct method The sample with the sulphide fixed is treated with NS at pH 5.2 in the presence of EDTA, then sulphanilic acid is added and sulphide is spectrophotometrically determined under the conditions described. The additon of chlorate (if necessary) prevents the interference of sulphites, as is discussed below in the interference study.

Beer's law is obeyed in the range 0.8–8.0 $\mu g.ml^{-1}$. The optimum concentration range for the effective determination of sulphide by Ringbom's method is 1.0–6.0 $\mu g.ml^{-1}$. The photometric sensitivity of the method is 0.0123 $\mu g.cm^{-2}$ and the molar absorptivity is $2.6 \times 10^{-2}\,l.mol^{-1}.cm^{-1}$.

The reproducbility of the procedure was determined by running 10 samples, each containing 3.6 $\mu g.ml^{-1}$ of sulphide ion in the final test solution. At this concentration level, the variation coefficient did not exceed 1.2 %.

Distillation method In order to assess possible analytical applications in coloured samples or samples not entirely free from suspended solids, or in order to achieve

Table 2 Effect of diverse ions on the direct spectrophotometric determination of sulphide[a]

Ion added	*Tolerance limit* ($\mu g.ml^{-1}$)
Anions	
Chloride, bromide, acetate	2000
Sulphate	1000
Nitrate, carbonate	500
Tetraborate, arseniate. orthophosphate, citrate, tartrate	200
Cyanide	150
Iodide, oxalate, thyocianate	100
Thiosulphate	50
Sulphite	6
Nitrite	4
Cations	
Na(I), K(I)	2000
Cd(II)	120
NH_4(I)	100
Ca(II), Mg(II)	50
Mn(II)	30
Cu(II), Zn(II)	5
Fe(III)	2.5

[a] Amount of sulphide taken: 1.5 μg.ml^{-1}.

preconcentration to attain greater analytical sensitivity, it appears that a separation of sulphide before determination may be necessary. The sulphide is distilled from acidic medium (phosphoric acid) as hydrogen sulphide which is collected on zinc acetate at pH 5.2.

The calibration graph was prepared between 0.4 to 4.0 μg.ml^{-1} using 200 ml of sample. For samples with lower concentrations of 0.2 to 2.0 μg.ml^{-1}, another calibration graph was prepared using 400 ml of sample. The coefficient of variation calculated for 10 analyses was 2.0% for samples containing 2 μg.ml^{-1} of sulphide.

Interference study In order to establish the suitability of the method for sulphide determination in water, the effect of some ions on both the direct and distillation methods were studied. An error of 2% in the absorbance reading was considered tolerable. Determinations were carried out in the presence of major constituents of water and frequent trace elements. The tolerance limits for the direct method are shown in Table 2. The major interferences were caused by anions as sulphite and nitrite which also react with NS. The addition of chlorate was found to prevent sufficiently the interference of sulphite and up to 6 μg.ml^{-1} could be tolerated when 2 ml of 0.5 M chlorate solution are added to the "already formed" suspension of ZnS in waters with intermediate contents of sulphite. For nitrite, the tolerance limit is not likely to be exceeded in any of the analysed waters.

Other sulphur-containing anions such as thiocyanate, thiosulphate and sulphate can be tolerated in greater amount, which is of analytical interest. Therefore, the relative amounts of thiosulphate, iodide and cyanide are greater than those

Table 3 Determination of sulphide in sewage effluents

Sample	*Sulphide found* ($\mu g.ml^{-1}$)[a]	
	Proposed method	*Methylene blue method*
A (untreated wastewater)	$0.98^{b} \pm 0.03$	$0.94^{c} \pm 0.03$
B (untreated wastewater)	$0.74^{c} \pm 0.01$	$0.71^{c} \pm 0.03$
C (treated wastewater)	$0.59^{c} \pm 0.2$	$0.58^{c} \pm 0.02$
D (treated wastewater)	$0.47^{c} \pm 0.02$	$0.47^{c} \pm 0.02$

[a] Average of three separate determinations.
[b] Direct determination without distillation.
[c] Determination with previous distillation.

tolerable in the methylene blue method. Anions such as chlorate, iodate and periodate, which cause the oxidation of sulphide, also interfere, especially if sulphide would not be fixed with Zn(II). However, if these oxidants are present in a sample, it is unlikely that any sulphide will be present. In other words, examination of these incompatible ions as interferences in this method becomes unnecessary.

Next, the effect of diverse cations was tested. Cations which form soluble sulphides can be tolerated in a large excess. Cations which react with sulphide to form precipitates repress the liberation of sulphide from the fixed ZnS and they interfere to some extent: Cu(II) and Zn(II) can be tolerated in a 5-fold excess, and Fe(III) in a 2.5-fold excess. Cd(II) is an exception because it can be tolerated in a 120-fold excess. On the other hand, to prove the effectiveness of EDTA as dissolving and masking agent, samples to which no Zn(II) or EDTA had been added showed significantly higher interferences for these cations; for instance, a 0.2-fold excess for Cd(II), Zn(II) and Cu(II), and only a 0.1-fold excess for Fe(III) could be tolerated.

The possible interference of anions such as Br^-, I^-. Cl^-, $C_2O_4^{2-}$, HPO_3^{2-}, SO_3^{2-}, CH_3—COO^-, CN^- and SCN^-, which are likely to be carried over by distillation, was investigated for the distillation method. The tolerance limits of these anions under the distillation conditions were very similar to those reported in Table 2. These results show that this procedure is highly selective.

Analysis of Sewage Effluents

The proposed procedures were applied successfully to the determination of trace amounts of sulphide both in untreated and treated water samples from a sewage treatment plant involving primary sedimentation. The results are given in Table 3, together with those obtained by the methylene blue method. Depending on the characteristics of the samples, the proposed method was applied directly or after previous distillation. That is, the direct method was applied to sample A and the distillation method to samples B, C and D, with sulphide contents below the calibration range of the direct method. The methylene blue method, however, was

Table 4 Characteristics of the methylene blue and of the NS/sulphanilic acid method

	Method	
	Methylene blue	*Proposed method*
λ_{max} (nm)	670	470
Optimum pH	0.9 N H_2SO_4	4.0–6.5
Molar absorptivity ($l.mol^{-1}.cm^{-1}$)	34000	26000
Range of Beer's law ($\mu g.ml^{-1}$)	0.02–20	0.8–8.5
Accuracy[a] (%)	±10	±0.6
Variation coefficient (%)	[b]	±1.2
Interferences ($\mu g.ml^{-1}$)		
NO_2^-	0.2	4.0
SO_3^{2-}	200.0	6.0
$S_2O_3^{2-}$	5.0	50.0
CN^-	[c]	150.0

[a]Calculated from the mean compared with the theoretical value.
[b]Not reported.
[c]Interferes, but quantitative result not reported.

not applicable to any sample because the presence of interfering substances prevented the formation of the blue colour and distillation had to be applied to all samples to remove these unknown interferences. The results showed that the accuracy of the determinations of sulphide is satisfactory.

CONCLUSIONS

The suitability of the sulphide/NS/sulphanilic acid system for the development of two accurate, selective and sensitive methods for determining small amounts of sulphide has been demonstrated. The use of distillation in a preconcentration and separation step separates sulphide from the major interfering ions. The results obtained with the proposed methods compare well with those of the standard methylene blue method. The standard method is more sensitive, but it seems to be less selective and accurate (Table 4). According to Gustavson,[13] the yield of methylene blue in the standard method is only about 65% of the theoretical and, besides, the rate of colour formation is highly dependent on the concentration of sulphide. Also, temperature influences the reaction rate and the temperature of standards and samples should be maintained within ±3 °C. Moreover, the amount of sulphuric acid added critically affects the final absorbances obtained by the methylene blue method.[18]

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