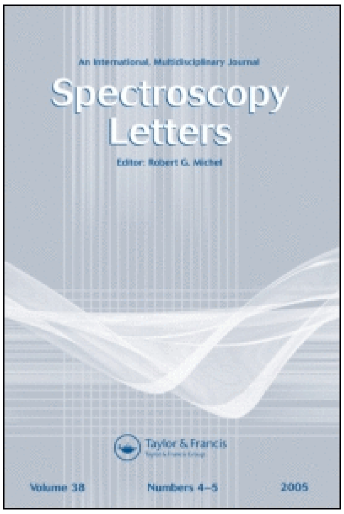

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On Line Dissolution of ZnS For Sulfide Determination in Stabilized Water Samples with Zinc Acetate, Using Spectrophotometry by Methylene Blue Method

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ON LINE DISSOLUTION OF ZnS FOR SULFIDE DETERMINATION IN STABILIZED WATER SAMPLES WITH ZINC ACETATE, USING SPECTROPHOTOMETRY BY METHYLENE BLUE METHOD

Keywords : On Line Dissolution, Sulfide, Stabilization, Spectrophotometry.

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ABSTRACT

Stabilization of sulfide as zinc sulfide is a strategy widely used in batch analysis of this ion in water. A FIA/spectrophotometry system to determine sulfide in stabilized water samples is proposed in this paper. The methodology is based on the formation of methylene blue by the reaction of H_2S with a mixture of Fe^{3+} solution and N,N-dimethyl-p-phenylenediamine

(DMPD) in acidic medium. In the system, the sample (480 μL) containing stabilized sulfide (as ZnS slurry) is injected in a carrier stream formed by mixing acidic Fe^{3+} and DMPD. In the reactor coil of 1280 μL, the sulfide is drifted by acid used in the preparation of solutions, releasing H_2S that reacts with Fe^{3+} and DMPD forming methylene blue. The absorbance is measured at 662 nm. The performance of the FIA system was optimized in relation to chemical and flow parameters. The stability of the solutions were studied throughout the period of the experiment. The results did not show any loss of sulfide over a 7 day period. However, in complex matrices an analysis by using the standard addition method is recommended. The analysis of effluent sample through the time showed good agreement between the results obtained each day. The developed system presented the following figures of merit: detection limit of 50 μg L^{-1}; RSD of 6% at 0.5 μg mL^{-1} (using ultrasonic homogenization) and analytical throughput of 60 samples per hour.

INTRODUCTION

Sulfide is a specie which can be found in low concentrations in anoxic natural waters. In these conditions its concentration can reach the magnitude of 100 μg mL^{-1}. Its behavior, in natural aquatic environments, is usually dependent on the climatic conditions and generally is present as the monoacid sulfide ion [1]. The oxidation of organic matter and reduction of sulfate ion are the greatest source of sulfide for domestic sewage waters. The sulfide ion is quite toxic for aquatic plants and animals.

According to APHA[2], two methods can be used for determination of sulfide in waters: the first is the spectrophotometric method, based on the formation of the methylene blue by the reaction that occurs between hydrogen sulfide and DMPD in the presence of iron (III). After the reaction, the use of ammonium phosphate is recommended in order to eliminate the iron (III) excess. This method can be applied in water samples ranging from 0.1 to 20 μg mL^{-1}, although its ideal range has been established as 0.1 - 2.0 μg mL^{-1}. Concomitants such as thiosulphate and other strong reducing agents can decrease the rate of formation of the colored product. Also, in high concentrations of sulfide the reaction becomes slow. The wavelength employed was 664 nm and the accuracy was 10 %. The second method recommended by APHA is a titrimetric method, which is based on the titration of sulfide with standard iodine solution in acidic medium, forming elementary sulfur. This procedure is recommended in samples where sulfide concentration is higher than 1 μg mL^{-1} and solutions where interferents are not present. The precision of this method is better than 0.1 μg mL^{-1}.

Several procedures using continuous flow were proposed for the determination of sulfide in water. Several analytical techniques such as chemiluminescence [3], ion selective electrodes [4,5], molecular emission in cavity detector [6], gas diffusion and potentiometry [7], fluorimetry [8], indirect AAS [9] and gas diffusion with amperometry [10] were employed in previous work. However, most of these methods were not used for the analysis of real samples. In the literature, there is no known citation of any work employing continuous flow and stabilization of the sulfide prior to analysis.

Legget et al [11] were the first to automatize, by flow injection analysis, the determination of sulfide. In the developed system, the samples were introduced in a carrier formed by iron (III) chloride and DMPD, in HCl medium. The analytical throughput was 210 samples per hour and the linear range of the method was 1 - 45 μg mL^{-1}. The wavelength used was 662 nm.

They studied the interferents and concluded that sulfite and thiosulfate were tolerated. The method studied was not applied for the analysis of real samples.

Rios et al [12] employed the same reagents for the determination of sulfide by reverse FIA. An analytical range of 0.5 - 5.0 μg mL^{-1} was used, with an observed precision of 0.7 % at 2 μg mL^{-1}. Strong interferences of nitrite and metallic cations were found. The analytical throughput of 48 samples per hour was calculated.

Kurzawa [13] investigated a procedure for determination of sulfur (II) compounds (including sulfide) based on the induced effect of these substances on the reaction between iodine and azide. Relatively good sensitivity was obtained (concentrations up to 200 μg mL^{-1} could be determined) but strong interferences were observed due to presence of others sulfur compounds. Kanson [14] developed the catalytic method based on the reaction cited above, in continuous mode. In this system, concentrations until 32 μg mL^{-1} could be determined by injection of 5 μL of sample. The authors related problems in reagent stability, depending on the concentrations of iodine and sodium azide. The methods were not applied in real sample analysis.

Sonne and Dasgupta [15] developed a methodology for simultaneous analysis of several species containing sulfur, including sulfide. The acidified sample yields H_2S which reacts with sodium nitroprusside in alkaline medium, after gas diffusion through the membrane. An indirect method, based on the drift reaction of sulfide with p-hidroximercurybenzoic acid in the presence of dithizone was also employed, by Yaqoob et al., for sulfide determination [16]. Little interferences were observed and the system operated at analytical throughput of 90 samples per hour. The detection limit calculated was 0.32 μg mL^{-1} and the precision was 0.7 % at 32 μg mL^{-1}. This methodology was not applied in real samples either.

In another work, Kuban et al. [17] suggested a procedure to determine sulfide after permeation of H_2S through the silicone membrane. They adopted a spectrophotometric detection, using nitroprusside and methylene blue methods. The sample, being acidified, releases H_2S, that after the permeation, is continuously collected by an alkaline solution in a handle of stationary sampling, before the spectrophotometric measurements. In this method, the preconcentration factor depends on the volume of sample that passes through the system.

Cassella and Santelli [18] developed a FIA system to determine sulfide in natural waters using its reaction with sodium nitroprusside in alkaline medium. In this work, preconcentration techniques were not employed. However, instead of others authors, the methodology was applied in analysis of real samples. Good results were obtained operating with analytical throughput of 80 samples per hour and limit of detection of 70 μg L^{-1}.

Review papers can also be found in the literature [19-22]. In one of the most interesting reviews, Chen et al [22] compared several FIA systems used for sulfide determination.

REAGENTS AND SOLUTIONS

Deionized water was used in the preparation of the solutions and reagents. The standard solution of 1000 μg mL^{-1} S^{2-} was prepared by dissolving of 7.50 g of $Na_2S.9H_2O$ in water containing a lentil of NaOH and the volume was filled up to 1 liter. This solution was periodically standardized using the iodometric method. The analytical solutions were prepared immediately before the use by dilutions of the stock solution.

N,N'-dimethyl-p-phenylenediamine (DMPD) was prepared by dissolving 0.4212 g in 1000 mL of 1 mol L^{-1} HCl. This solution is stable for 10 days.

Fe^{3+} solution was prepared by dissolving 3.5312 g of $NH_4Fe(SO_4)_2.12$ H_2O in 1000 mL of 1 mol L^{-1} HCl.

All samples were prepared containing 300 μg mL^{-1} Zn^{2+} (as acetate salt), stored in polypropylene flasks and maintained in a refrigerator until analysis.

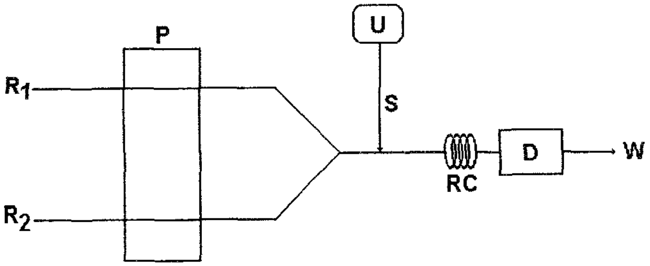
FLOW SYSTEM

The flow injection system studied is depicted in Fig 1. In this simple manifold, the sample (480 μL) is injected in a carrier stream formed by merging two reagents, 3.5×10^{-3} mol L^{-1} DMPD solution pumped at 1.4 mL min^{-1} and 7.2×10^{-3} mol L^{-1} Fe^{3+} solution pumped at 1.4 mL min^{-1}. The mixture is continuously introduced in the 1280 μL reactor coil and, after the color development, the absorbance is measured at 662 nm using a 80 μL flow cell. Peak height was used in all measurements.

Sample and analytical solutions containing 0.5 – 2.5 μg mL^{-1} were always kept in a ultrasonic bath in order to homogenate the slurry formed and improve the reproducibility of the signals.

APPARATUS

A Micronal B - 342 II spectrophotometer, equipped with a Hellma flow cell (178-010-OS), setting at 662 nm was used, coupled to an ECB - Equipamentos Científicos do Brasil, model RB-210, x-y recorder. A Desaga-



R_1 - 3.5 x 10^{-3} mol L^{-1} DMPD prepared in 1 mol L^{-1} HCl, 1.4 mL min^{-1}.

R_2 - 7.2 x 10^{-3} mol L^{-1} Fe^{3+} prepared in 1 mol L^{-1} HCl, 1.4 mL min^{-1}.

P - peristaltic pump.

U - ultrasonic bath.

S - sample, 640 µL.

RC - reactor coil, 1280 µL.

D - detector, 662 nm.

W - waste.

Fig. 1. Optimized FIA system.

PLG peristaltic pump, furnished with silicone tubes, was employed to propel all solutions. A home made proportional comutator [23] was used for sample introduction. All connections were made using glass materials. Manifold was built up with polypropylene tubes of 0.8 mm bore.

EVALUATION OF CHEMICAL AND FLOW PARAMETERS

Since its creation, FIA systems have been employed in order to decrease human participation in the analytical processes, decreasing contamination risks and increasing the analytical throughput without loss of sensitivity. Optimization of the FIA systems is a strategy to improve the performance, being applied on chemical and flow variables. The main objective of this work was to study the viability of the determination of sulfide in stabilized water samples and its behavior with the time.

Chemical Variables

The chemical variables studied were: concentration and acidity of DMPD, concentration and acidity of Fe^{3+}solution and influence of the ionic strength on the analytical signal. The influence of the concentration of DMPD on the absorbance was investigated varying this parameter in the range of 1.2 x 10^{-3} mol L^{-1}– 12.4 x 10^{-3} mol L^{-1}. Best results were obtained between 3.1 x 10^{-3} mol L^{-1} – 3.7 x 10^{-3} mol L^{-1}. The concentration of 3.5 x 10^{-3} mol L^{-1} was chosen for further experiments. After this, the acidity of the DMPD solution was tested preparing this solution in different concentrations of HCl solution. Solutions with 0.5 mol L^{-1} until 2.9 mol L^{-1} were tested and the signals were almost constants between 0.5 – 1.0 mol L^{-1} with a soft increase in concentrations near to 1.0 mol L^{-1}. Therefore, the DMPD solution was always prepared in 1.0 mol L^{-1} HCl.

At the same way, the parameters cited above were investigated for Fe^{3+} solution. The concentration of $Fe^{3+}$was studied in a range of 2.9 x 10^{-3} mol L^{-1} – 22 x 10^{-3} mol L^{-1}. The better condition was obtained at a concentration of 7.2 x 10^{-3} mol L^{-1}. Acidities were studied in order to maximize the process of dissolution of the ZnS formed. The higher absorbance signals were observed when the Fe^{3+} solutions were prepared in a 1.0 mol L^{-1} HCl solution.

The aim of this investigation was to apply the developed methodology in water sample analysis, thus the influence of the ionic strength was studied.

These experiments were carried out using a 1.0 μg mL^{-1} sulfide solution prepared in NaCl solutions with different concentrations. This way, the effect of the ionic strength was investigated from 0.1 to 0.9 mol L^{-1} of NaCl. For the range of 0.1 to 0.5 mol L^{-1} no signal variation was verified. From 0.5 mol L^{-1} to 0.9 mol L^{-1} the signal decreases achieving an absorbance loss of 10 % for the highest salinity tested.

FIA variables

The effect caused by change of the flow rate was studied. For DMPD, the influence of flow rate was studied in a range of 0.86 - 1.62 mL min^{-1}. In the case of Fe^{3+}, flow rate was investigated in a range of 0.43 - 1.59 mL/min. Both solutions showed similar results, with the best signals in a flow rate of 1.4 mL min^{-1} for DMPD and 1.4 mL min^{-1} for Fe^{3+}. In higher flow rates, a slight decrease of the signal was observed because of the increase of the sample zone dispersion effect.

The analytical signal increases with increasing injection volume up to 640 μL, above which it decreases, probably because of the difficulty of the reagent reaching the central zone of the sample plug when this is too large, causing double peaks. A volume of 480 μL was chosen as a compromise between sensitivity, sample consumption and sample frequency.

The influence of the volume of the reactor coil was also studied. This parameter was varied between 640 and 1280 μL. The reactor coil that yielded maximum absorbance signal was 1280 μL. Shorter volumes resulted in an incomplete reaction, with lower signals, while greater volumes showed lower signals because the effect of dispersion exceeded the increase observed due to evolution of the reaction.

STABILIZATION STUDY

A stabilization study was performed with three kinds of samples: (1) deionized water; (2) saline water and (3) an industrial effluent water. This study consisted of the addition of Zn^{2+} to the sample containing sulfide resulting in the formation of insoluble ZnS. Therefore, the loss of sulfide as H_2S, or by oxidation forming SO_4^{2-} is minimized.

The objective of this study was to evaluate the viability of the determination of sulfide as ZnS and the influence of the time in this determination. The experiments were performed measuring the following ratio:

$$R = S_{Zn} / S$$

Where S is the slope of analytical curve in deionized water prepared immediately before the measurements and S_{Zn} is the slope of the analytical curve in samples with and without (no stabilized sample) addition of Zn^{2+}.

Measurements of R were done daily, during 168 hours, employing standards (in concentrations between 0.5 and 2.5 μg mL^{-1}) prepared in the different matrices. The results obtained for the three kinds of samples are shown in Fig. 2. It was observed that, in water, sulfide was not lost in solutions containing Zn^{2+}, confirmed by a value of R which was always near to 1, during the entire time of the experiment. This observation proves the efficiency in the fixation of sulfide as ZnS and its dissolution inside the FIA system.

In industrial effluent water, the behavior of R was almost the same. There was only a little increase in R during the experiment. However, it can be noted that the loss of sulfide was not observed, confirmed by the constant value of R through the test time. The increase of R was probably caused by a

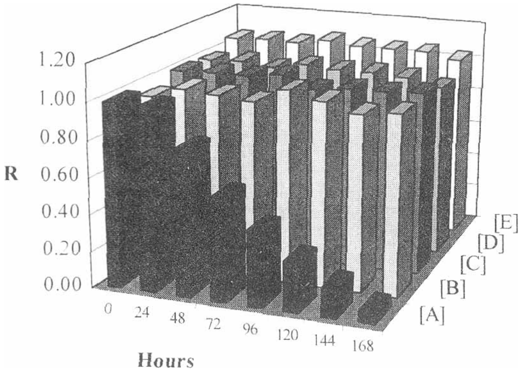


Fig. 2 - Stabilization study with on line dissolution of slurry sample. R is ratio S_{Zn}/S; [A] sulfide in deionized water; [B] sulfide + 300 μg mL^{-1} Zn (II) in saline water (7.0 ‰); [C] sulfide + 300 μg mL^{-1} Zn (II) in saline water (35.2‰); [D] sulfide + 300 μg mL^{-1} Zn (II) in deionized water and [E] sulfide + 300 μg mL^{-1} Zn (II) in industrial effluent water.

matrix effect. In saline solutions there was a slight decrease in the value of R, also caused by matrix effects. This result is coherent with that observed in the study of the influence of the ionic strength on the absorbance signal. On the other hand, the solutions without Zn^{2+} showed a great loss of sulfide, identified by the decrease of R value after 24 hours.

In order to reach results with better precision it was necessary to study the influence sample mixing on its behavior. Mechanical mixing and ultrasonic mixing were used. The ultrasonic mixing resulted in less variable signal and was selected as the preferred method.

INTERFERENCES

The influence of various ions on the analytical signal was tested. It was chosen for those usually found in natural waters such as Mg^{2+}, Ca^{2+}, PO_4^{3-},

CO_3^{2-}, HCO_3^-, SO_4^{2-}, NO_3^-, and Br^-. They were tested in concentrations 1,000 times higher than sulfide. No relevant interference was observed.

Additionally some reducing agents such as thiosulphate and nitrite were tested as potential interferents anions. Thiosulphate was investigated in concentrations between 10 and 100 μg mL^{-1}, and the results showed that the methodology can be applied for samples containing a maximum of 40 μg mL^{-1} (four times better than that related for batch procedure [2]). For concentrations higher than 40 μg mL^{-1} the signal decreases continuously. Nitrite was also tested in concentrations between 5 and 100 μg mL^{-1}. However, strong interferences were verified, allowing the determination of sulfide in the presence of only 5 μg mL^{-1} of nitrite. Analytical signal decreases dramatically in concentrations higher than that. Ammonium was tolerated up to 100 μg mL^{-1}.

Presence of metallic cations in the samples can influence the analytical signal through in two ways: (1) increasing or decreasing the reaction rate, and (2) interfering in the dissolution process (by formation of very insoluble sulfides with the interfering ions).

In order to verify the effect of these cations on the reaction rate, a simple experiment was performed. After stabilization of the samples (containing 1 μg mL^{-1} of S^{2-} and zinc acetate), a small amount of the studied cation was added and the signals were measured. No interference was observed for the following cations in the ratios (in relation to the sulfide concentration) indicated: Mn(II) 1:30, Ni (II) and Fe (III) 1:10, Cd(II) 1:5 and Pb(II) 1:1. The analytical signal was strongly affected by the presence of Cu(II) at any ratio tested. Obviously, Zn(II) was not tested as an interferent because of its role as a stabilization agent.

By changing the addition order of the reagents, it was possible to investigate the influence of the metallic cations on the dissolution process. In this case, the interfering metal ion was added to the sample before the addition of the zinc acetate (at the same concentrations used in previous experiments). The signals then were measured after 30 minutes and compared to the situation where no metallic cations were present. Unstable signals were obtained and quantitative measurements could not be performed.

However, the two situations above are not a critical problem because the levels of these metallic cations in natural waters are lower than that tested. Also, we can consider that the cations cited, if present in the environment studied, are already precipitated as sulfides and the main objective of this work was to develop a methodology to determine the sulfide soluble fraction. In all the samples studied the sulfide was present in its free form as S^{2-} or HS^-.

DETERMINATION OF SOLUBLE SULFIDE IN WATERS

The flow system described was good enough to determine sulfide in an industrial effluent water with reasonable sensitivity. Employing the stabilization strategy was possible to realize these determinations in a space of time of 7 days without loss of analyte. This fact was confirmed taking the sulfide concentration obtained at zero hour as the reference and applying the two-tailed t test in order to verify possible differences between the results obtained through the time. As can be seen in Table 1, at a significance level of 0.05 no differences were found among the results. In saline waters it was not possible to verify the presence of the sulfide due to very low concentrations.

Results obtained in the analysis of the real sample are shown in Table 1, as well as the results obtained in recovery tests. These results show

Table 1: Result obtained, by standard addition method, in each day of the experiment in a sample of industrial effluent water.

Time (hours)	Sulfide found ($\mu g\ mL^{-1}$)*	t-value (P=0.05)	Recovery (%)
0	2.47 ± 0.13	4.30**	105
24	3.12 ± 0.52	2.10	106
48	2.51 ± 0.26	0.24	105
72	2.25 ± 0.12	- 2.15	108
96	2.63 ± 0.15	1.40	106
120	2.47 ± 0.20	0	106
144	2.20 ± 0.15	- 2.36	106
168	2.37 ± 0.20	- 0.73	103

* n=3 for all experiments.

** critical value of t.

influence of the matrix in the determination of sulfide by methylene blue/stabilization method. Therefore, the sample must be analyzed using the standard addition method. Under optimum conditions, linear calibration graphs were obtained for sulfide concentrations between 0.5 and 2.5 $\mu g\ mL^{-1}$. A typical equation for the method was $A = 0.158\ [S^{2-}(\mu g\ mL^{-1})] + 0.003$, $r = 0.998$, where A is the peak height absorbance. The limit of detection achieved was 50 $\mu g\ L^{-1}$ and the RSD was always better than 6 % at 0.5 $\mu g\ mL^{-1}$.

CONCLUSIONS

This paper is the first report that describes the use of stabilization strategies based on ZnS precipitation and its on-line dissolution, in analysis of sulfide in a flow system. The FIA system developed is a simple, rapid and inexpensive method to determine sulfide in water samples, solving the most common problem in this analysis: the lost of sulfide after its sampling.

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