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APPLICATION OF ATOMIC FLUORESCENCE SPECTROMETRY TO THE
DETERMINATION OF SULFIDE ION IN SEWAGE WATERS

KEY WORDS: Atomic fluorescence spectrometry,
sulfide, flame photometry.

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ABSTRACT

Atomic fluorescence spectrometry and direct flame photometry are evaluated as alternative methods for the determination of inorganic sulfide in municipal sewage. The sulfide is volatilized as H_2S from the sewage influent or effluent sample, which has been stabilized by a 0.05 M sodium ascorbate buffer. Both flame spectrometric methods are more sensitive than the standard colorimetric method, but quantification is easier for the atomic fluorescence method. The latter technique has a wide linear dynamic range and is unaffected by a gradual increase in the residual H_2S level in the system. The atomic fluorescence signal is also unaffected by the presence of volatile hydrocarbons in the sewage. The results obtained with the fluorescence method agree well with those obtained with the standard method, while the flame photometric results are low. Studies on the effect of metal ions on the fluorescence signal indicate that the method determines "total sulfide".

INTRODUCTION

Inorganic sulfide is commonly present in industrial wastes and municipal sewage waters as a result of bacterial reduction of sulfate and decomposition of organic sulfides. The total sulfides include a mixture of insoluble metal sulfides such as those of iron, chromium, lead, nickel, and copper, while dissolved sulfide consists of H_2S and HS^- , depending on the pH of the solution. Hydrogen sulfide escaping into the atmosphere from sewage and waste waters, even at concentrations of 0.1ppm or less, can create an odor nuisance. When present in concentrations above 500 ppm, it can cause immediate loss of consciousness and death in 30 min. This gas is also known to cause serious corrosion problems in concrete sewers, because it is oxidized in the presence of oxygen, water and bacteria to form sulfuric acid on the walls of the sewer lines¹. Because of the toxicity of H_2S and the environmental and industrial problems it may create, there exists a need for a direct, rapid and sensitive method for the determination of low concentrations of inorganic sulfide in sewage and waste samples.

Sulfide has been determined by a number of methods. The most commonly employed analytical techniques are direct colorimetry on zinc acetate stablized solutions using N,N-dimethyl-p-phenylene diamine, known as the methylene blue method, and the titrimetric iodine method². The methylene blue method measures sulfide concentrations of 0.02-20 ppm, while the iodine method is applied when sulfide concentration is above 1.0 ppm. Even though the above techniques are considered reference methods, they both suffer interferences from reducing agents and even high concentration of sulfide itself². Alternate direct spectrophotometric methods have been developed^{3,4}.

Other techniques include indirect atomic absorption spectrometry⁵, differential pulse polarography⁶, electron-capture gas chromatography after

derivatization of sulfide as bis(pentafluorobenzyl) sulfide⁷, and gas chromatography with flame photometric detection⁸⁻¹⁰. Several other investigations have involved the use of silver sulfide ion-selective electrodes¹¹⁻¹³, iodide ion-selective electrodes¹⁴, or cadmium sulfide membrane electrodes¹⁵.

Despite the number of publications concerning the determination of sulfide in various media, none of the methods is completely satisfactory on the basis of sensitivity, selectivity, and speed of analysis. In this paper, we wish to report on the use of atomic fluorescence spectrometry (AFS) for determining the concentration of inorganic sulfide in sewage water. Previously, it was shown that AFS can be used to determine nanogram quantities of gaseous H_2S ¹⁶. Although it was shown that AFS is less prone to quenching interference of hydrocarbons than is flame photometry, the AFS system was not evaluated on real samples. The relatively high concentrations of volatile hydrocarbons in raw sewage¹⁷ makes the determination of H_2S volatilized from such samples an appropriate test of the selectivity of the AFS detector.

In the study described here, sewage samples were collected in sodium ascorbate buffer, and the sulfide in the sample was volatilized and determined as H_2S by both AFS and flame photometry. The effect of various metal ions common in municipal sewage on the recovery of sulfide was determined. The efficacy of the ascorbate buffer, relative to zinc acetate solution, for the preservation of sulfide samples was investigated. The AFS measurements, as well as the flame photometry results, were compared with the standard methylene blue method.

EXPERIMENTAL

Apparatus. The excitation source employed for all fluorescence measurements is a 1000 watt PRA illuminator system. The AFS spectrometer components, as

modified for far ultraviolet measurements, and the sparging tube used for volatilization of the H_2S have been described earlier¹⁶. The monochromator and the lamp housing were purged with nitrogen at a flow of approximately 2 l/min for at least two hours prior to turning the system on. The optimal flame and spectrometer conditions previously determined¹⁶ were used, but the sparging argon flow rate was reduced to 0.50 liter/minute, in order to minimize foaming of sewage samples.

The flame photometric studies were performed on the same experimental apparatus, optimized for observation of the 372 nm S_2 emission. In order to allow the sampling system to equilibrate, 400 ppm H_2S in nitrogen (Scott Specialty Gases) was continuously introduced into the apparatus for one half hour prior to running samples.

Reagents. All chemicals were ACS reagent grade and used without further purification. Aqueous solutions were prepared with doubly distilled, deionized water.

Ascorbate buffer, 0.1M: 44 g of L-ascorbic acid was dissolved in one liter freshly boiled water. 400 ml of the ascorbic acid stock solution was transferred to a one liter volumetric flask. 100 ml of 1.0 M NaOH was added and the solution was made up to the mark with freshly boiled water. The pH of this solution was approximately 12. For some metal ion interference studies, 18 g of EDTA was added to the sodium ascorbate solution and the pH was adjusted to 12 with 1.0 M NaOH before final dilution.

Sulfide Stock Solution: Approximately 0.25 g of washed sodium sulfide crystals were dissolved in 250 ml of 0.1 M NaOH and the solution was stored in a dark bottle. The exact concentration of this standard was determined by iodometric titration immediately prior to dilution. Working sulfide standards were prepared daily by dilution in 0.05 M ascorbate buffer.

Sample Collection. Sewage samples were obtained at the East Bank Sewerage and Treatment Plant, New Orleans, LA. Influent samples were collected from about

four feet below the surface of the influent channel, and effluent samples were obtained from an effluent water pipe. For the methylene blue method, samples were collected in 250 ml amber bottles with the addition of zinc acetate and sodium hydroxide, according to the standard procedure². Samples for the fluorescence and emission studies were collected in 500 ml amber bottles after placing 250 ml of 0.1 M ascorbate buffer in each bottle prior to collection. Fluorescence and emission samples were later diluted as needed with 0.05 M ascorbate.

Procedure. Sulfide determinations on all the samples were performed on the day of collection. The methylene blue method was performed according to a standard procedure². For the AFS and flame photometric methods, a 25.00 ml aliquot of the sample was placed in the sparging tube and purged for one minute prior to the addition of 0.4 ml of 6 M HCl. The resulting buffered solution (pH = 4) was sufficiently acidic to rapidly volatilize H_2S , while retaining HSO_3^- in solution. Both peak height and peak area were recorded on an integrating recorder (Houston Instruments Model B5218-11).

RESULTS AND DISCUSSION

Choice of Sulfide Preservative. The standard method of preservation of trace sulfide solutions is to precipitate the sulfide as the zinc salt. The resulting suspension is quite stable. Unfortunately, this method could not be used in conjunction with AFS determination. Although a fluorescence signal was observed upon acidification of the suspension, foaming of the sample caused severe irreproducibility. Since sodium ascorbate had been used by others^{11,12} to stabilize sulfide samples, and we had used it with success in our preliminary investigation¹⁷, all subsequent work involving volatilization of H_2S was performed on solutions stabilized with 0.05 M ascorbate.

The stability of sulfide in the ascorbate solution, compared to sulfide in the usual zinc acetate preservative, was investigated. Duplicate 0.50 ppm

sulfide standards were prepared in both media and stored for various periods up to six days in tightly closed amber glass bottles. All solutions were analyzed vs. freshly prepared standards, the ascorbate solutions by AFS, and the zinc acetate samples by the methylene blue method. The results are shown in Figure 1. The stability of a 0.50 ppm sulfide standard in 2 M NaOH is shown for comparison. These results indicate that sulfide stabilized with ascorbate is stable for several days, as long as it is not exposed to air.

Wilson, et al.¹² repetitively analyzed a single sulfide sample stabilized with sodium ascorbate over a period of six days. They reported a slow decomposition of the sample, which contained a rather high (750 ppm) sulfide concentration. We repeated that experiment using a 0.50 ppm sulfide solution, and obtained results similar to theirs. Nevertheless, we feel that the results shown in Figure 1 more accurately represent the efficacy of stabilization with ascorbate, since samples are rarely opened between collection and analysis. For the sewage samples analyzed in this study, analyses were always performed within several hours of collection, since bacterial action could affect the sulfide concentration over longer periods.

Effect of Metal Ions. Several transition metals commonly found in municipal sewage precipitate sulfide. The results of a study of the effect of these metals on the AFS signal obtained for a 0.25 ppm sulfide solution are shown in Table 1. The metal ion concentrations are all four times the levels normally expected in a 1:1 diluted sewage sample¹⁸. As can be seen, the only interferences are from lead and copper. The effect of lead was eliminated by the addition of EDTA to the ascorbate buffer, while the copper interference was unaffected. Lower levels of these metals caused proportionally lower amounts of interference.

These results demonstrate that the AFS method, using ascorbate without EDTA, determines what has been defined as "total sulfide", i.e., sulfide which

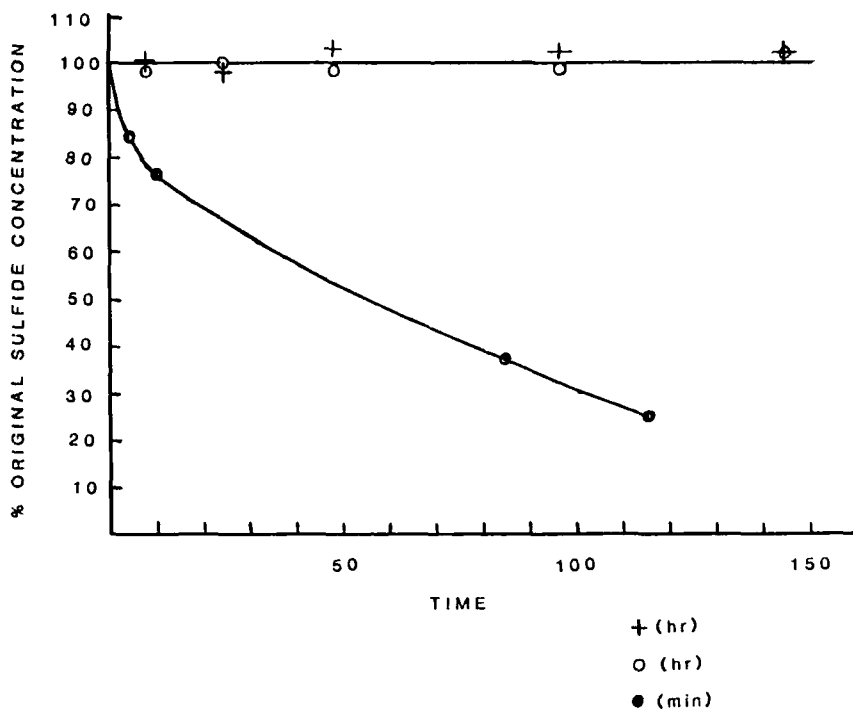


Figure 1. Stability of 0.50 ppm sulfide ion in (+) 0.003 M zinc acetate + 0.006 M NaOH, (O) 0.05 M ascorbate solution (pH= 12), (●) 0.01 M NaOH.

is liberated upon acidification of a sample. Sulfide which is not liberated upon acidification, such as copper sulfide, is of less concern and is not determined in most methods². Lead sulfide is insoluble at pH=4, however, it does not significantly affect the sulfide concentrations found in most sewage influent samples. If lead is of concern, EDTA should be added to the ascorbate preservative.

Comparison of Methods. Under the conditions employed in this study, the AFS method was found to have a linear dynamic range from its detection limit of about 1.5 ppb to 1.5 ppm, using peak area measurements. Although peak height

TABLE 1

Metal Interferences on Volatilization of Sulfide^a

<u>Metal Ion</u>	<u>Metal Concentration</u>	<u>AFS Peak Area^b</u>
None	---	100
Fe ²⁺	4.0	100
Ni ²⁺	0.8	101
Cr ³⁺	1.4	101
Cd ²⁺	0.34	100
Zn ²⁺	2.8	100
Pb ²⁺	1.2	87 (98) ^c
Cu ²⁺	1.5	0 (0) ^c

^a Sulfide concentration 0.25 ppm.^b Average of three areas relative to area with no interferent.^c 0.05 M EDTA added.

was also linear for standards, it could not be used for the determination of sulfide in sewage samples, due to considerable variability of the peak width. This was attributed to suspended solids in the samples. The determination of sulfide by direct flame photometry was severely limited by this phenomenon. In the flame photometric method, the square root of the photocurrent is proportional to the concentration of sulfur compound in the flame. Since our instrumentation did not allow the direct recording of the square root of the photocurrent, the peak area was not even approximately linear with respect to the sulfide concentration. Instead, the following equation was employed:

$$I^{1/2}W = ac^2 + bc + d,$$

where I = the peak maximum (nanoamps),

W = the peak width at $1/4$ maximum (corresponding to $1/2$ the maximum sulfide concentration) (seconds),

and c = sample sulfide concentration (ppm).

TABLE 2

Comparison of Methods for Sulfide Determination

	<u>AFS</u>	<u>Flame Photometry</u>	<u>Methylene Blue</u>
Sulfide Found (ppm)	2.90	2.63	2.88
% R.S.D. within sample	2.5	2.4	2.5
% R.S.D. between samples	2.2	5.9	4.4
% R.S.D.(Total)	2.5	3.4	3.5

The quadratic term in the above equation generally represented about 12% of the linear term at the 1 ppm level.

The results obtained with the AFS and photometric methods were compared to that of the methylene blue method by collecting three influent samples for each method and analyzing each sample in triplicate. The results are shown in Table 2. There is no significant difference in the precisions of the three methods at the 95% confidence level.

Not evident in the results of the analysis of variance is a significant positive drift in the response of the flame photometric detector. For example, when six sequential replicates of a single sample were analyzed by photometry, the calculated concentration increased monotonically from 2.50 ppm to 2.70 ppm vs. standards run before the replicates. A positive drift in flame photometric analysis has been observed previously¹⁹, and is attributed to an increasing residual H_2S concentration in the system. This causes an increased response to a given amount of sulfide, due to the quadratic nature of the response¹⁹. An increase in the background level was observed over a period of time in both AFS and flame photometry experiments, despite extensive preconditioning of the device with H_2S . It was of no concern in the AFS

TABLE 3

Sulfide Concentrations in Sewage Samples (ppm)^a

<u>Date</u>	<u>AFS</u>	<u>Methylene Blue</u>
3/29/83	1.43 (0.04)	1.48 (0.05)
5/1/83	3.92 (0.08)	3.79 (0.13)
5/1/83 ^b	0.100 (0.004)	0.097 (0.014)

^a standard deviation in parentheses.

^b Effluent Sample.

measurements, since the background could simply be subtracted from the signal. In order to obtain accurate results with flame photometry, a pair of standards had to be run after every three samples.

The samples used in the analysis of variance study were all collected from the influent channel over a period of a few minutes. Table 2 indicates that the mean concentration for the flame photometry determination was significantly different ($t=11.4$ for 16 degrees of freedom) from the concentrations found using the other two methods. The AFS and methylene blue results agreed well with each other. The reason for the lower value obtained with flame photometry is not known, although flame photometric signals have been shown to be quenched more than AFS response by hydrocarbons¹⁶. It is possible that the volatile hydrocarbons present in sewage¹⁷ affected the value found by photometry. In any event, considering the other problems encountered using direct flame photometry, it was abandoned as a possible method of analysis.

The AFS and methylene blue methods were compared for three other samples, two influents and one effluent. The results, shown in Table 3, verify good agreement between the two methods. For the effluent sample, the relative standard deviation of the methylene blue method was poor, due to the low

concentration. The detection limit of the methylene blue method was 0.02 ppm. The AFS method also allowed a somewhat faster throughput rate, since no time was required for sample treatment or color development. Approximately twenty samples could be determined per hour by AFS.

CONCLUSIONS

Atomic fluorescence is a viable method for the determination of total sulfide in sewage, after volatilization of the analyte as H_2S . 0.05 M sodium ascorbate is effective in stabilizing trace sulfide. Although requiring more sophisticated instrumentation than the standard methylene blue method, AFS is more sensitive and somewhat faster. AFS may be preferred over the methylene blue method in certain circumstances. These would include the analysis of samples containing reducing agents or high amounts of solid, and the determination of very low sulfide levels. More important, the results of this study indicate that AFS is capable of accurately determining the sulfur content in a fairly complex gaseous matrix. Although direct flame photometry is simpler experimentally, it suffers from a drifting response and yields significantly lower results than the other two methods.

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