

Low Parts per Billion Determination of Sulfide by Coulometric Argentometry

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Present methods for the determination of sulfide in wastewater are hindered by poor detection limits and extensive sample pretreatment. A less problematic method has been developed with a method detection limit of $2.5 \mu\text{g L}^{-1}$. With this technique, sparged hydrogen sulfide is precipitated in an acetate-supporting electrolyte by electrogenerated silver ions. Analysis of base-preserved samples was performed with no pretreatment other than volumetric dilution. Metals, halides, and nitrogen-base salts were studied as possible interferences to the method. Direct comparisons with the standard methylene blue method were made for both municipal and industrial wastewaters. The present method was found to be far less inhibited by sample turbidity.

Introduction

Sulfide [$\text{S}(-\text{II})$], the most reduced form of sulfur, is formed in wastewater by the action of anaerobic bacteria on organic matter. Numerous problems are associated with its presence in sewers and organic waste treatment systems. The least damaging but certainly most readily perceived problem is nuisance odor. Because sulfide is readily protonated, wastewaters containing sulfide have a high potential to emit volatile H_2S into the air. Odor of this species can be detected even when sulfide concentration is as little as 0.01 mg L^{-1} in cold water, and odor from water containing as much as 0.1 mg L^{-1} is definitely offensive (1). A related problem is the toxicity of H_2S , which is approximately the same as cyanide gas, with an LC_{50} of 700 ppm (2). Deaths have resulted from levels exceeding only 0.03% in the air, and more widespread health problems such as reduced lung function have been documented for chronic exposure to lower levels (3). Finally, broad economic problems are associated with the corrosiveness of sulfide and H_2S toward cement-bonded materials. The problem is most severe when solution conditions change from anaerobic to aerobic. Corrosion occurs when H_2S is converted to sulfuric acid by aerobic bacteria that adhere to concrete surfaces. The acid can attack the lime component (CaO) of the cement bonding and convert it to the more soluble and brittle gypsum (CaSO_4).

Clearly the level of sulfide in industrial and municipal wastewaters has a tremendous impact on public acceptance and safety as well as the longevity of concrete infrastructure. Unfortunately, the standard methods presently used to analyze for sulfide are difficult to automate and suffer from

numerous chemical interferences and solution turbidity (4, 5). More importantly, without extensive pretreatment (3), these methods generally detect sulfide only if it is present in quantities greater than 1 mg L^{-1} . These detection limits are not sufficient to screen for low levels that can lead to nuisance odor or chronic corrosion.

Electrochemical methods for the determination of sulfide have consisted of amperometry and coulometric argentometry (CA). The amperometric methods (6–8) have used gas-permeable polymer membranes to separate the volatile hydrogen sulfide. This volatile species was then detected electrochemically through mediated oxidation with ferri-cyanide as the redox mediator. CA involves sparging volatile species of sulfide into various electrolytes, including cyanide for aqueous samples (9), phosphoric acid for solids (10), and ammonia and sodium hydroxide for thioacetamide (11). An attempt has also been made to determine the amount of sulfur in organic compounds by reducing SO_2 with triiodide, using almost an equivalent system as the one in this paper (12). For safety reasons, the method for aqueous samples is no longer applicable.

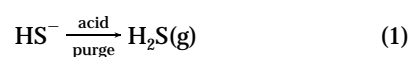
This paper describes a semi-automated method that can quantify sulfide content in wastewaters to low ppb levels with nearly a 500-fold linear range. The method is relatively free of chemical interferences and is not affected by solution turbidity. Extensive testing on real samples from food processing and municipal wastewater treatment facilities have demonstrate the utility of the method.

Experimental Section

Reagents. All reagents were used as received. Sodium sulfide ($\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, 99.9%) was purchased from Aldrich (Milwaukee, WI). Potassium biiodate ($\text{KH}(\text{IO}_3)_2$, purified), potassium iodide (KI, reagent), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, ACS reagent), and sodium hydroxide (NaOH, reagent) were obtained from Fisher Scientific. Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$, analytical grade) and ammonium phosphate dibasic ($(\text{NH}_4)_2\text{HPO}_4$, analytical grade) were received from Mallinckrodt, Inc. EM Science supplied both hydrochloric acid (HCl, 35.5%) and sulfuric acid (H_2SO_4 , 95–98%). Iodine (I_2 , ACS reagent) and *N,N*-dimethyl-*p*-phenylenediamine oxalate [$(\text{NH}_2\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2(\text{COOH})_2$] were purchased from Matheson, Coleman, and Bell Manufacturers and TCI, respectively. All aqueous solutions were prepared with 18 M Ω cm Milli-Q reagent water (Millipore Corp.).

Instrumentation. Sulfide analysis was performed with a home-modified automatic argentometric titrator (model DX-25) marketed by Tekmar Co. (Cincinnati, OH) for the determination of volatile organic chlorides (Figure 1). Originally, the DX-25 included a sample introduction assembly, an aqueous sparging column similar in design to purge systems used for GC sampling (13), a tube furnace for combustion of volatile organics, and an argentometric titration cell containing two pairs of electrodes. For the determination of aqueous sulfide, volatile hydrogen sulfide formed within the sparging column (eq 1) was directly transferred into the titration cell where it was precipitated by silver ion (eq 2) generated by a silver wire electrode (eq 3).

sparger



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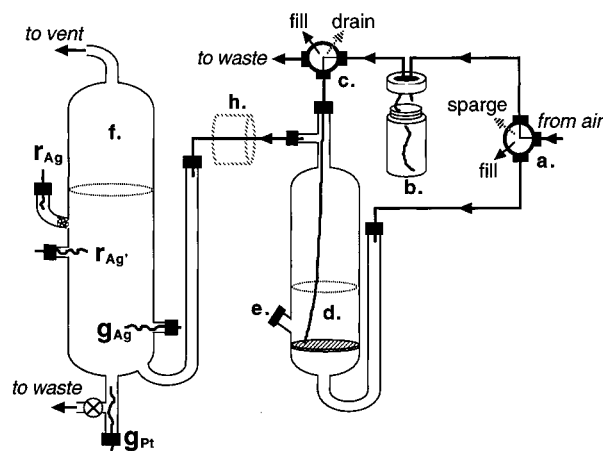
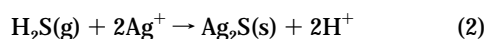


FIGURE 1. Diagram of sample introduction and titration apparatus. Parts are (a) air distribution valve, (b) 40-mL EPA sample vial, (c) liquid distribution valve, (d) sparge column, (e) silicone rubber septum, (f) titration vessel, (g) silver ion generation electrodes (Ag and Pt), (h) combustion furnace (not used), (r) silver ion reference electrodes.

titration cell



generator electrode



Patented electronic circuitry of the DX-25 (14) automatically monitored the Ag^+ precipitation by H_2S , electronically, integrated in the total charge passed for $\text{Ag}^+(\text{aq})$ generation and displayed the charge in units of nanograms of chloride. Amounts of sulfide precipitated by the DX-25 were calculated by eq 4.

$$\text{ng S(-II)} = (\text{ng Cl}^-) \times \frac{(32.06 \text{ g mol}^{-1} \text{ S(-II)})}{(35.45 \text{ g mol}^{-1} \text{ Cl}^-)} \times \frac{(1 \text{ mol Ag}^+/1 \text{ mol Cl}^-)}{(2 \text{ mol Ag}^+/1 \text{ mol S(-II)})} \quad (4)$$

Field Sampling and Preparations. Grab samples were obtained from wastewater treatment facilities of local food processing industries and municipal lift-stations. Samples were collected in high-density polyethylene (HDPE) bottles with minimum aeration and were preserved by adjustment with 1 N NaOH to a pH greater than 9. All samples were transported and stored under refrigeration (4 °C) until analyzed, usually within 48 h. Quality control was established by performing duplicate collections every fourth sample and blank collections every 10th sample.

Laboratory Procedures. The titration cell was rinsed daily and filled with fresh electrolyte solution consisting of 70 parts glacial acetic acid to 30 parts deionized water. A fresh sulfide standard was prepared daily [ca. 80 ppm S(-II), from $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$] and standardized by iodometric titration according to standard method (4). This stock solution was diluted with 0.01 M NaOH (to retain a pH greater than 9) to prepare calibration standards.

Wastewater samples were introduced as 20.00-mL aliquots in a 25-mL EPA vial. In some cases, flocculent samples were filtered through a glass fiber solids filter to remove suspended solids including insoluble sulfides. These solids had the potential to become lodged in the transfer tubing. Each sample was transferred to the sparging column where its pH was adjusted to less than 5 with 1.0 mL of 6 N sulfuric acid

TABLE 1. Calibration Data for Linearity and Recovery Determination of Standard Solution

| actual (ng of S(-II)) | obsd (ng of S(-II)) ^a | | | av (ng of S(-II)) | Δ% ^b | % RSD |
|--------------------------|----------------------------------|------|------|----------------------|-----------------|-------|
| 6365 | 4724 | 4937 | 4818 | 4826 | 24.2 | 2.21 |
| 4773 | 3806 | 3783 | 3806 | 3798 | 20.4 | 0.00 |
| 3580 | 2952 | 2838 | 3002 | 2931 | 18.1 | 2.87 |
| 1989 | 1709 | 1702 | 1780 | 1730 | 13.0 | 2.49 |
| 796 | 761 | 775 | 755 | 764 | 4.0 | 1.34 |
| 699 | 510 | 534 | 531 | 525 | 24.8 | 6.68 |
| 466 | 319 | 333 | 320 | 324 | 30.4 | 1.63 |
| 373 | 229 | 236 | 230 | 231 | 38.0 | 2.41 |
| 233 | 126 | 126 | 112 | 121 | 48.1 | 2.49 |
| 0 | -10 | -9 | -8 | -9 | | 11.11 |

^a Data converted by eq 3. ^b Δ% = [(act - obs)/act] × 100.

(injected through a syringe port). At this pH, 99% of the sulfide was converted to volatile H_2S . In some cases, an antifoaming agent (Antifoam B Silicone Emulsion, Baker) was also injected to inhibit excessive bubble formation within the sparger and to prevent any liquid carryover to the titration cell. Automatic sparging and titration were initiated, and integration of the generator electrode current yielded the amount of $\text{Ag}^+(\text{aq})$ produced in units of nanograms of Cl^- . Following each analysis, the sample was drained from the sparger and the sequence was repeated. For quality assurance, standards were analyzed every fifth sample, and blanks were analyzed if cross-contamination of the transfer tubing or sparging column was suspected. Cross-contamination was extremely rare and only occurred with highly concentrated ($>1 \text{ mg L}^{-1}$) and flocculant samples.

Results and Discussion

Linear Range. The modified DX-25 showed linear calibrations for sulfide standard samples through a range of $1.8 \mu\text{g L}^{-1}$ (LOD) to ca. $320 \mu\text{g L}^{-1}$. Results for a typical calibration run are given in Table 1. This upper limit of the range was not limited by a decrease in instrument sensitivity. Rather, the maximum sulfide concentration that could be analyzed without dilution was approximately $450 \mu\text{g L}^{-1}$. This upper limit of the linear range was imposed by the 4.5 digit display of the DX-25 ($<20\,000 \text{ ng of Cl}^-$). However, repeated analysis of near ppm solutions also caused rapid degradation of the electrode surfaces within the titration cell because of accumulated silver sulfide. In these situations, frequent changes of electrolyte and recalibration were necessary. Standards were analyzed in triplicate and generally yielded calibration slopes of 0.6–0.8 with correlation coefficients exceeding 0.95. For the calibration data given in Table 1, the slope was 0.778 with a correlation coefficient of 0.987.

Detection Limits. A method detection limit (MDL) for standardized samples was found to be 50 ng of S(-II) ($2.5 \mu\text{g L}^{-1}$ for 20.00-mL sample). This level was determined by analyzing seven split samples of a standard solution that was 2–3 times the concentration expected for the MDL (13). The standard deviation of the readings was multiplied by 3.14 and the calibration slope to give the MDL in actual ng of S(-II). Limit of detection (LOD) and limit of quantitation (LOQ) were determined from 20 blank samples that were analyzed over a period of 2 days. The LOD established at $2(1.64) \times$ the blank standard deviation and LOQ established at $10 \times$ the blank standard deviation were 17 ng of S(-II) ($0.85 \mu\text{g L}^{-1}$ for 20.00-mL sample), and 36 ng of S(-II) ($1.8 \mu\text{g L}^{-1}$ for 20.00 mL), respectively.

Sample Throughput. The average rate of analysis was governed by the number of samples requiring dilution or filtration. For sub ppm solutions, since neither of these pretreatments was generally necessary, the maximum

TABLE 2. Interferences to Analysis of S(-II) by CA Method

| component | concn (mg L ⁻¹) | blank reading (C) S(-II) | spike recovery (%) |
|--|-----------------------------|--------------------------|--------------------|
| NaCl | 1000 | 0 | 92.4 |
| NaBr | 1000 | 0 | 92.4 |
| NaI | 1000 | 0 | 86.7 |
| Na ₂ CO ₃ | 1000 | 0 | 91.8 |
| Na ₂ C ₂ O ₄ | 1000 | 0 | 88.0 |
| KNO ₃ | 1000 | 0 | 136.2 |
| KNO ₂ | 100 | 0 | 0.0 |
| Co(C ₂ O ₂ H ₃) ₂ | 10 | 0 | 0.0 |
| Cu(C ₂ O ₂ H ₃) ₂ | 10 | 0 | 0.0 |
| FeCl ₃ | 10 | 0 | 37.6 |
| FeCl ₂ | 10 | 0 | 59.6 |
| Mn(C ₂ O ₂ H ₃) ₂ | 10 | 0 | 87.5 |
| Ni(C ₂ O ₂ H ₃) ₂ | 10 | 0 | 64.3 |
| Pb(SO ₄) | 1 | 0 | 52.0 |
| Zn(C ₂ O ₂ H ₃) ₂ | 10 | 0 | 113.9 |

throughput was greatest at 6 h⁻¹. Analysis of ppm solutions was slowed considerably for samples requiring filtration (ca. 1–2.5 h⁻¹) but was only moderately affected for samples requiring only dilution (4–5 h⁻¹).

The general trend of more rapid throughput for more dilute samples was in direct contrast to most standard methods of S(-II) analysis. In these methods, dilute samples are generally concentrated by precipitation with zinc acetate. The subsequent steps of quantitative filtration and redissolution of ZnS requires considerable time that severely limits throughput for these methods.

Interferences. Three categories of common environmental matrix components were investigated with the method, and the results are summarized in Table 2. The tested components included acids that could precipitate Ag⁺, common nitrogen-based salts, and metal ions that could precipitate sulfide.

In the first case, 1000 mg L⁻¹ solutions of chloride, bromide, and iodide salts were analyzed without S(-II) present but did not yield readings above normal blank levels. These constituents also did not affect S(-II) spike recovery. Although HCl, HBr, and HI are all volatile species, they are also strong electrolytes and do not associate in solution. More basic anions that could associate proton, volatilize, and precipitate Ag⁺(aq) include carbonate, cyanide, and oxalate. Of these, carbonate demonstrated no interference since its acid form only exists in solution. Oxalate also showed no interference because of its limited volatility in acid form. Although cyanide was not tested for reasons of safety, its known basicity and volatility in acid form suggest a severe interference.

A surprising level of interference was detected for nitrate and nitrite salts. In the former case, it was apparent from blank measurements that a volatile component was carried to the titration vessel that was formed by attack of 6 N H₂SO₄. It was not possible to identify this component or to assess if its action in the titration cell was to precipitate silver or to diminish the current efficiency of silver ion production. In the case of nitrite, spike recovery of sulfide was poor, indicating a decomposition reaction. Nitrite is known to be an effective oxidant toward other anions such as oxalate and iodide under acidic conditions. Upon considering the complex nature of nitrogen oxide redox chemistry, the mechanism for the nitrite and nitrate interferences were not investigated, as they were not crucial to the ultimate conclusions of the work.

Interference from metal ions that precipitate with sulfide was generally observed, but the severity of the interference varied with each metal. The most stable metal sulfides could

TABLE 3. Postanaerobic Food Processing Wastewater^a

| sample | dilution | ng of S(-II) | concn |
|------------------|----------|--------------|--------------------------|
| stage 1 | 1/1000 | 46.0 | 6.82 mg L ⁻¹ |
| | 1/1000 | 233.0 | 44.83 mg L ⁻¹ |
| | 1/1000 | 2.7 | 2.90 mg L ⁻¹ |
| stage 2 | 1/100 | 51.5 | 0.73 mg L ⁻¹ |
| | 1/100 | 100.0 | 1.71 mg L ⁻¹ |
| | 1/100 | 136.0 | 1.50 mg L ⁻¹ |
| stage 3 | | 44.5 | 6.68 µg L ⁻¹ |
| | | 52.5 | 7.41 µg L ⁻¹ |
| | | 64.5 | 8.49 µg L ⁻¹ |
| stage 4 (finish) | | -15.0 | <MDL |
| | | -13.0 | <MDL |
| | | 8.0 | 3.38 µg L ⁻¹ |

^a Correspondence between site and sulfide concentration.

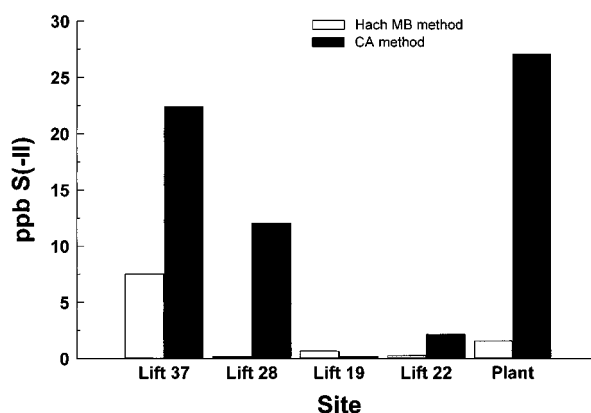


FIGURE 2. Sulfide content at sanitary sewer liftstation sites. Comparisons with methylene blue (MB) method are shown.

not be detected by our method because these solids would not be solubilized even under acid treatment in the sparging column. These metal ions included Co²⁺ and Cu²⁺. For some metal sulfides, particularly NiS, MnS, and ZnS, solubilization with concentrated H₂SO₄ in the sparging column was possible. Pretreatment of solutions with alkaline antioxidant reagent (AAR), used for dissolution of zinc-preserved solutions, did not yielded appreciably higher spike recoveries.

Real Samples. Local wastewaters were analyzed to assess the accuracy and precision of the method for real matrices. Wastewaters were selected from sites that posed severe environmental impact, either through nuisance odor or through corrosive degradation of treatment facilities.

The first sites analyzed were wastewater treatment cells from two local food processing companies. Both treatment facilities operated with anaerobic digesters upstream from aerobic holding ponds. The anaerobic wastewater contained sulfide at very high concentrations (>100 mg L⁻¹). Wastewater from downstream aeration ponds contained lower amounts of sulfide that were below the detection limits of the standard methods. However, because of the low MDL of the present method, it was possible to assess relative sulfide changes as the wastewater neared finishing (Table 3).

The second sites analyzed were municipal sanitary sewer lift-stations that suffered from odor and corrosion problems. The samples taken from these sites were also tested by the Hach MB field kit, a colorimetric test based on the methylene blue method (Figure 2). The CA method showed consistently higher results than those obtained by the MB test. This consistent bias was probably due to solution turbidity. When the standard method MB (4) test was performed on blind, clarified standards and compared to results obtained for the

TABLE 4. Sulfide Analysis Comparison of Coulometric Argentometry (CA) and Methylene Blue (MB) Using Blind Standards

| | MB | | CA | |
|-----------|-----------------------------|-------|-----------------------------|-------|
| | av ($\mu\text{g L}^{-1}$) | % RSD | av ($\mu\text{g L}^{-1}$) | % RSD |
| unknown 1 | 34.64 | 13.96 | 34.80 | 3.71 |
| unknown 2 | 15.75 | 6.71 | 15.59 | 2.44 |
| unknown 3 | 25.50 | 7.17 | 26.83 | 0.56 |

same solution by CA, the two methods showed no significant difference (Table 4).

Conclusions

The present method combines the sensitivity of silver-based coulometric titration with the separating and concentrating ability of purge-and-trap. High selectivity for sulfide is controlled by volatility within an upstream sparging column as well as by extremely low solubility with silver ion within a downstream titration cell. For these reasons, the method provides routine detection limits that are much lower than most standard methods and maintains relative freedom from interference by turbidity and common matrix components.

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