Automated Determination of Sulfide as Hydrogen Sulfide in Waste Streams By Gas-phase Molecular Absorption Spectrometry

Les Ebdon*[a], Steve J. Hill[a], Mohammad Jameel[a], Warren T. Corns[b] and Peter B. Stockwell[b]

[a] *Department of Environmental Sciences, University of Plymouth, Plymouth, UK PL4 8AA*
[b] *PS Analytical Ltd., Orpington, Kent, UK BR5 3HP*

The gas-phase molecular absorption spectrometric method for determining sulfide was applied to the determination of sulfide in waste water using a fully automated system. The instrumentation utilizes a commercially available vapour generator and an absorption cell placed in the optical path of an atomic absorption spectrometer set at 200 nm. A sulfide anti oxidant buffer (SAOB) consisting of sodium hydroxide (0.5 mol l^{-1}), sodium tetrahydroborate (0.2 mol l^{-1}) and sodium citrate (0.2 mol l^{-1}) was found to have advantages in terms of shelf-life over existing SAOB formulations. A gas–liquid separator was designed that also assisted in the transport of the hydrogen sulfide, generated by hydrochloric acid (0.6 mol l^{-1}), to the absorption cell. The limit of detection was 0.13 mg l^{-1} of sulfide and the calibration was linear up to 100 mg l^{-1}. Of 16 ions tested for interference, at a 50-fold excess, only copper, lead, zinc and arsenic gave serious interference problems. The method was applied to the determination of sulfide in waste waters and good agreement was found with the stabilized iodine titration procedure. Spike recoveries from the waste water ranged between 97 and 101%. Unattended operation allowed the analysis of up to 90 samples per hour.

Keywords: *Sulfide determination; automated analysis; gas-phase molecular absorption spectrometry; hydrogen sulfide generation with tetrahydroborate; waste water samples*

Sulfide is a constituent of waste streams arising from a variety of industrial operations. Sulfide salts (*e.g.*, sodium hydrogensulfide) may also be added to industrial waste streams in order to control the levels of toxic metals (*e.g.*, mercury, lead) discharged into the environment, since many metal sulfides are insoluble and precipitate out in the waste stream. There are limits on the total level of sulfide permitted in waste discharges in most countries because of toxicity, capacity to remove dissolved oxygen and capability to produce hydrogen sulfide. Hence the needs for sulfide control are obvious. Clearly an on-line instrument that is capable of directly determining sulfide levels in waste streams is desirable and would allow the optimization of sulfide treatment of waste streams. Given the growing popularity of the PS Analytical system for measuring mercury levels on-line using vapour generation, it was suggested that a similar on-line continuous vapour generation system for sulfide was worthy of investigation and development.

One of the earliest and best known methods for sulfide determination is the colorimetric Methylene Blue method developed by Johnson and Nishita.[1] Hydrogen sulfide was trapped in zinc acetate or an ammoniacal cadmium chloride solution, where it was fixed as zinc sulfide in the former or cadmium sulfide in the latter instance. Under suitable conditions, this trapping solution was reacted with *p*-aminodimethylaniline in the presence of iron(III) ions (usually as the chloride) to develop the Methylene Blue colour.

Sulfide determination can also be achieved by iodimetric titration.[2] This is based on the reaction

$$H_2S + I_2 \rightarrow S + 2H^+ + 2I^-$$

Direct titration of the sulfide can be carried out; however the best procedure to attain an accurate result is to add an excess of iodine followed by back-titration of this excess with thiosulfate.

Both methods described above offer good sensitivity and accuracy but also have disadvantages.[3] The intensity of the Methylene Blue colour can be affected by temperature and strong reducing agents that can prevent its formation. The efficiency of the trapping solutions varies with the rate of sampling and the time interval for colour development can be as much as 3 h, depending on the concentration of hydrogen sulfide. With the iodimetric method there is the possibility of the oxidation products from the hydrogen sulfide (which are almost always present), namely sulfite and thiosulfate, reacting with the iodine to give erroneous results. Both methods do not lend themselves easily to automation.

Automated procedures for the determination of sulfide have not been widely reported. A flow injection variation of the Methylene Blue method has been described by Leggett *et al.*[4] and more recently Arowolo and Cresser[5] described an automated system for the determination of sulfide using gas-phase molecular absorption spectrometry (GPMAS). Sulfide ions were reacted with 3 mol l^{-1} hydrochloric acid and the released hydrogen sulfide was swept into an absorption cell in the light path of an atomic absorption spectrometer. The absorbance at 200 nm was measured using a deuterium hollow-cathode lamp.

We have further developed the system of Arowolo and Cresser[5] but utilizing a variation on their chemistry, to allow the routine determination of sulfide. The system was assessed for its suitability for on-line instrumentation. Results from a full interference study that was undertaken are presented, and also results for the application of the method to the analysis of waste water samples.

Experimental

Sulfide Antioxidant Buffer (SAOB) Solution

A prerequisite for sulfide determination is the need to stabilize the analyte in a SAOB solution,[6] as sulfide in solution is slowly oxidized by the ambient atmosphere with ease. This normally consists of an alkaline solution (which raises the pH and prevents loss of sulfide as hydrogen sulfide), a reductant (to inhibit oxidation of sulfide by surrounding air) and a ligand salt (to complex any trace metal impurities which may possibly catalyse the oxidation reaction). The stability of SAOB solutions has been investigated by Glaister *et al.*[7] Fresh SAOB solutions were prepared daily.

Initially, the SAOB solution chosen by Arowolo and Cresser[5] was used (2 mol l^{-1} sodium hydroxide, 0.2 mol l^{-1} ascorbic acid and 0.2 mol l^{-1} EDTA). However, it was found that the EDTA precipitated upon mixing with the acid reagent and tended to block the delivery line between the valve and gas–liquid separator. It was therefore replaced with sodium citrate as a complexing agent. In later experiments, sodium tetrahydroborate was chosen as the reductant, mainly because of its relatively high reducing power in comparison with ascorbic acid. It can also be stabilized in milder alkaline conditions. This in turn means that the reaction to hydrogen sulfide can be achieved using an HCl reagent of lower concentration—an important consideration for an on-line system as reagents would normally be prepared weekly in bulk for the system and thus preparation is cheaper and safer if concentrations are kept as low as possible.

Reagents

Distilled, de-ionized water (Milli-Q; Waters, Milford, MA, USA) was used to prepare all reagent solutions. Sulfide antioxidant buffer (SAOB) was initially prepared from 2 mol l^{-1} sodium hydroxide [AnalaR, BDH (Merck), Poole, Dorset, UK], 0.2 mol l^{-1} L-ascorbic acid (99+% ACS reagent, Aldrich, Milwaukee, WI, USA) and 0.2 mol l^{-1} sodium citrate (99+% ACS reagent, Aldrich). In later experiments the SAOB concentrations were 0.5 mol l^{-1} sodium hydroxide and 0.2 mol l^{-1} sodium tetrahydroborate (99+% ACS reagent, Aldrich) while the citrate concentration was kept the same as before. The initial concentration of hydrochloric acid [AnalaR, BDH (Merck)], used was 3 mol l^{-1} and this was modified to 0.6 mol l^{-1} in later experiments using the tetrahydroborate SAOB.

A 500 mg l^{-1} sulfide stock standard solution was prepared daily by weighing 1.875 g of sodium sulfide nonahydrate (98% ACS reagent, Aldrich) on an analytical balance and dissolving to 500 ml in 25% v/v SAOB solution. Working standard solutions were prepared from this solution in clean 100 ml calibrated flasks, at the appropriate calibration range, by serial dilution using 25% v/v SAOB solution.

Various solutions of cations and anions for the interference studies were prepared at either the 25 000 or 50 000 mg l^{-1} level using analytical-reagent grade salts.

Instrumentation

A schematic diagram showing the configuration of the fully automated system is shown in Fig. 1. A vapour generator (Model 10.004, PS Analytical, Orpington, Kent, UK) consisting of a pump, valve and borosilicate gas–liquid separator was interfaced to a cold glass absorption flow-through cell with quartz end windows *via* a Permapure dryer (PS Analytical). The glass absorption cell rested on the burner head of a Unicam (Cambridge, UK) SP9 atomic absorption spectrometer, aligned along the optical path of the spectrometer and held in place with Nichrome wire. A deuterium lamp was used to provide light at the analytical wavelength of 200 nm. The vapour generator was controlled using Touchstone software (Spinoff Technical Systems, Benfleet, Essex, UK) *via* a PC and a DIO card. The absorption signals were also interpreted and displayed on the computer using Touchstone software and a Spinoff A/D card. Final instrumental conditions are given in Table 1.

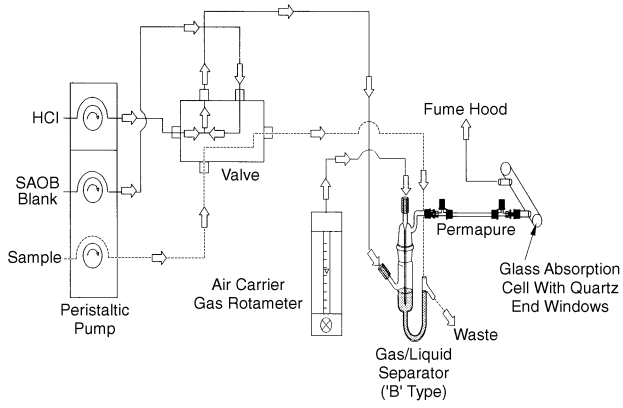

Fig. 1 Schematic diagram of instrumentation.

Procedure

Determination of sulfide was carried out using GPMAS. Essentially a solution of sulfide, stabilized in 25% v/v SAOB solution, was mixed in a gas–liquid separator with HCl to generate hydrogen sulfide. The gaseous product was stripped from the solution by a stream of air and introduced into the glass flow-through atom cell, where its absorbance was measured at 200 nm. The whole system operated on a continuous-flow principle. Initially, a 25% v/v SAOB solution was continuously pumped through a switching valve into a gas–liquid separator mixing with a stream of HCl. This allowed a baseline to be established. The valve was then electronically switched and the sulfide sample solution, also in 25% v/v SAOB solution (blank matched), introduced into the gas–liquid separator while the blank solution was pumped to waste. Once the hydrogen sulfide signal had reached the steady state, the valve was switched back to the blank solution, allowing the signal to reach the baseline again: the valve timings were set in the software so that a steady-state signal for hydrogen sulfide could be achieved before the valve switched back. It is recommended that argon or nitrogen is used as the carrier gas to obviate any possibility of explosions occurring if an air carrier gas is used together with the tetrahydroborate chemistry.

Results and Discussion

Optimization of Parameters

After initial establishment of the system, certain parameters were modified in order to observe their effect on the sensitivity of the system, measured as the peak height of the signal. Univariate searches were performed on the system using the initial chemistry and various components were investigated. The final conditions, considered to give the best response, are shown in Table 2.

The sensitivity increased dramatically when the gas–liquid separator was changed from type 'A' to 'B' (see Fig. 2). The

Table 1 Final instrumental conditions

Vapour Generator		Atomic absorption spectrometer	
Parameter	Value	Parameter	Value
Valve—			
Delay	10 s	Lamp	Deuterium
Rise	20 s	Current	10 mA
Measure	30 s	Wavelength	200 nm
Memory	40 s		
Carrier	Air, 200 ml min^{-1}	Bandpass	2 nm
Dryer	Air, 2 l min^{-1}	Burner height	5.0
Flow rates—			
HCl	2.8 ml min^{-1}	Background correction	Off
SAOB	7.6 ml min^{-1}		
Sample	7.6 ml min^{-1}		

essential difference between the two is that in the 'A' type device the headspace above the solution was purged with the carrier gas whereas in the 'B' type separator the carrier stream purged the solution in the separator. The resultant increase in sensitivity, by a factor of almost 10, was due to improved removal of the dissolved hydrogen sulfide in solution and more efficient transport to the atom cell. Increasing the sample flow rate with respect to the HCl flow rate also approximately doubled the sensitivity whereas increasing the bandpass from 2 to 10 nm showed no effect.

Fig. 3 shows that while the dryer gas flow does not significantly affect the absorbance of a 20 mg l^{-1} sulfide standard, decreasing the carrier gas flow resulted in an increase in the absorbance, which would be expected as this simultaneously decreases the dilution and increases the residence time of the hydrogen sulfide molecules in the flow-through absorption cell. Changing the lamp current showed no variation in the signal-to-background ratio. Replacing the Permapure membrane with a similar length of silicone-rubber tubing showed no improvement or degradation of the total sensitivity of the system. The dryer tube was retained to prevent problems from condensation in the absorption cell, since the above experiments confirmed that hydrogen sulfide was not lost through the drying membrane.

Table 2 Final system parameters

Parameter	Initial	Final
Bandpass/nm	2	2
Separator*	'A' type	'B' type
3 M HCl flow rate/ml min^{-1}	2.6	2.6
SAOB blank flow rate/ml min^{-1}	2.8	7.6
Sample flow rate/ml min^{-1}	2.8	7.6
Carrier gas flow rate/ml min^{-1}	300	200
Dryer gas flow rate/ml min^{-1}	750	750

* See text and Fig. 2.

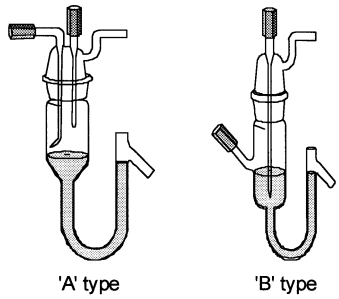

Fig. 2 Type 'A' and 'B' gas–liquid separator designs.

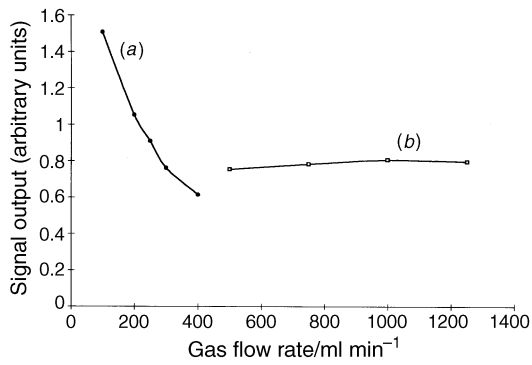

Fig. 3 Variation of analytical signal for 20 mg l^{-1} sulfide with (*a*) carrier and (*b*) dryer gas flows.

Comparison of the two Chemistries

As outlined above, it was felt that 2 mol l^{-1} sodium hydroxide and consequently 3 mol l^{-1} hydrochloric acid were concentrated reagents to use in unattended operation. It was necessary, however, to compare the performance of the new tetrahydroborate chemistry and more dilute hydrochloric acid with the previously published procedure. Therefore, a 50 mg l^{-1} sulfide solution was prepared in both SAOB solutions and the absorbance was measured over a period of 90 h. Fig. 4 shows the stability of a 50 mg l^{-1} sulfide standard in the initial and modified SAOB solutions over 90 h. The effectiveness of the tetrahydroborate chemistry in retaining the sulfide in solution in comparison with the ascorbate chemistry is clearly indicated. An interesting effect noticed when using the tetrahydroborate can be seen from the typical peak signals obtained from the two chemistries illustrated in Fig. 5, which show that the evolution of the hydrogen sulfide is faster when using the tetrahydroborate SAOB.

Interference Study

An interference study was conducted on both chemistries and the effects of several ions on a 10 mg l^{-1} sulfide standard are presented in Table 3. This interference study demonstrated some further advantages of the modified SAOB, which overcame any interferences observed from nitrite and sulfite compared with the ascorbate SAOB. Zinc seemed to affect the tetrahydroborate chemistry whereas it had no effect on the ascorbate SAOB.

Significant interference effects were seen from only a few ions. Arsenic, a hydride forming element, caused a major enhancement of the absorption signal using the tetrahydroborate chemistry but a suppression using the ascorbate chemistry. The enhancement was attributed to the generation of arsine (AsH_3), which will absorb at 200 nm. Using the tetrahydroborate chemistry, when a solution of arsenic was analysed without the addition of the sulfide a signal was observed confirming this.

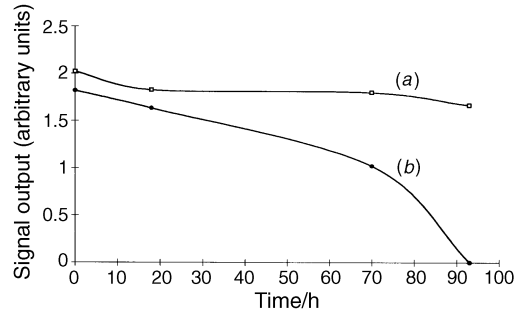

Fig. 4 Variation in output of a 50 mg l^{-1} sulfide solution in (*a*) tetrahydroborate and (*b*) ascorbate over SAOBs over 90 h.

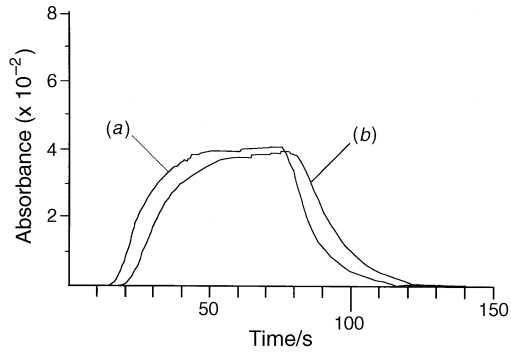

Fig. 5 Typical analytical signals for 20 mg l^{-1} sulfide solution in (*a*) tetrahydroborate and (*b*) ascorbate SAOBs.

Selenium, bismuth (and possibly antimony, although this forms a very insoluble sulfide) would also be expected to affect the signal similarly, but were not included in this interference study.

Severe suppressions by copper(II) and lead(II), which affected the analytical signal at both the levels tested (500 and 100 mg l^{-1}), were observed with both chemistries. As both metals form extremely insoluble sulfides [pK_{sp} (CuS) = 35.2, pK_{sp} (PbS) = 26.6], it is assumed that any free sulfide in solution will have precipitated as the respective metal sulphide. This is supported by the fact that dark precipitates were observed when the sulfide solutions were being spiked with the metals in preparation for the interference study.

The effect of various concentrations of copper(II) and lead(II) on the recovery of a 10 mg l^{-1} solution of sulfide is illustrated in Fig. 6. It shows that Cu^{II} commenced to affect the signal at about 1 mg l^{-1}, whereas Pb^{II} still interfered significantly even at the 1 mg l^{-1} level.

Detection Limits and Calibration

Both chemistries were assessed on the continuous-flow system with respect to limit of detection (LOD) and linearity. The LOD for the methods was calculated as three times the standard deviation obtained from 10 runs on a 0.2 mg l^{-1} sulfide standard solution. Using the ascorbate SAOB the LOD was 0.04 mg l^{-1} whereas it was 0.13 mg l^{-1} for the tetrahydroborate based chemistry. Although the ascorbate SAOB gave a lower LOD the tetrahydroborate chemistry was found to have a greater linear range, to > 100 mg l^{-1} compared with 60 mg l^{-1} for the ascorbate based chemistry. The tetrahydroborate system was also more suited to small samples, such as are encountered in flow injection methodology, because of its faster rise time. In practice, sample times of 10 s can be used in the continuous flow fully automated system described with this chemistry (and can further extend the linear range of the method).

Table 3 Results of interference study

Interferent	Interferent level/mg l^{-1}	Recovery (%) Ascorbate SAOB	Recovery (%) Tetrahydroborate SAOB
Cl^-	500	99	101
Br^-	500	98	99
I^-	500	99	101
NO_3^-	500	101	101
NO_2^-	500	196	98
	100	99	
SO_4^{2-}	500	99	101
SO_3^{2-}	500	> 200	106
	100	178	
PO_4^{3-}	500	101	98
CO_3^{2-}	500	100	96
Cu^{2+}	500	0	0
	100	0.1	25
Fe^{3+}	500	98	96
Mg^{2+}	500	100	102
Ni^{2+}	500	102	104
Pb^{2+}	500	45	0
	100	29	0
Zn^{2+}	500	101	16
	100		19
As^{3+}	500	43	> 200
	100	83	> 200

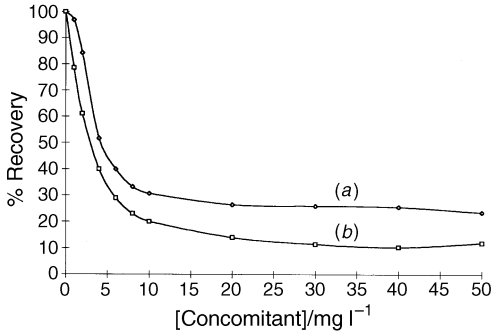

Fig. 6 Suppression of 10 mg l^{-1} S^{2-} by varying the concentrations of (*a*) Cu^{2+} and (*b*) Pb^{2+}.

Accuracy

The accuracy of the two chemistries was assessed by determining the level of sulfide in real waste water brine samples. Tables 4 and 5 present the results. While the composition of the samples was unknown at the time of analysis, the samples were analysed by the independent supplying laboratory by the iodine titration method and this is given as the 'Expected' value in Tables 4 and 5. Both of the chemistries assessed gave results that were not significantly different from those obtained by the independent laboratory. The continuous-flow method reported here appeared to give a much better precision of measurement.

Conclusions

The GPMAS method for the determination of sulfide published by Arowolo and Cresser[5] was adapted using a chemistry that

Table 4 Ascorbate SAOB results

Sample	Result/ mg l^{-1}	Recovery (%)	Expected*/ mg l^{-1}	Obtained†/ mg l^{-1}
A_1	2.04		14 ± 3	16.3
A_2	2.00		14 ± 3	16.0
A_3	1.99		14 ± 3	15.9
A_1 + spike‡	5.97	98		
A_2 + spike	6.01	100		
A_3 + spike	5.92	98		
B_1	1.19		11 ± 2	9.55
B_2	1.22		11 ± 2	9.75
B_3	1.21		11 ± 2	9.67
B_1 + spike	5.11	98		
B_2 + spike	5.11	97		
B_3 + spike	5.07	97		

* Result obtained by titration method. † Dilution corrected result (dilution factor = 8). ‡ Spiked at 4 mg l^{-1} S^{2-}

Table 5 Tetrahydroborate SAOB results

Sample	Result/ mg l^{-1}	Recovery (%)	Expected*/ mg l^{-1}	Obtained†/ mg l^{-1}
A_1	1.53		14 ± 3	12.3
A_2	1.51		14 ± 3	12.1
A_3	1.50		14 ± 3	12.0
A_1 + spike‡	3.67	107		
A_2 + spike	3.51	100		
A_3 + spike	3.60	105		
B_1	1.57		11 ± 2	12.6
B_2	1.36		11 ± 2	10.9
B_3	1.48		11 ± 2	11.9
B_1 + spike	3.52	98		
B_2 + spike	3.51	108		
B_3 + spike	3.52	102		

* Result obtained by titration method. † Dilution corrected result (dilution factor = 8). ‡ Spiked at 2 mg l^{-1} S^{2-}.

allowed easier automation. It was found to be relatively free from interferences. The method was validated with results obtained from real waste water samples, reported in Tables 4 and 5. The results obtained were in good agreement with the iodine titration method, within experimental error and allowing for some sample deterioration during transportation time. Recoveries between 97 and 108% were obtained from sulfide spikes.

The LOD for the method was estimated as 0.13 mg l^{-1} ($3\sigma_{n-1}$), based on ten runs on a 0.2 mg l^{-1} standard solution, and it was found to be linear up to at least 100 mg l^{-1}.

Owing to the faster evolution of the hydrogen sulfide determinand (Fig. 5), the chemistry is much better suited for automation. By using an autosampler and shortening valve times on the vapour generator, the system can achieve unattended analyses of up to 90 samples per hour. More important, because the chemistry makes use of reagents of low concentrations, it is appropriate for use in an on-line instrument.

The analytical requirements can be achieved in a similar manner to the on-line determination of mercury. The flow pattern required for the analysis is directly comparable with that for the on-line mercury analyser. Simply replacing the atomic fluorescence mercury detector with a molecular absorption detection system allows the unit to be used for sulfide monitoring in waste streams and the two systems can be used together to complement each other. Hence the original objective of the work has been realised.

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