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Project Summary

Modification of Methods 9030 and 9031 for the Analysis of Sulfide by Specific Ion Electrode

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Two OSW SW-846 methods (Method 9030 and 9031) used for the determination of sulfide have been modified to include the use of sulfide specific ion electrodes (SIE). Currently in both methods sulfide is converted to hydrogen sulfide and distilled into a scrubber solution for subsequent determination by iodometric titration. In the modified methods, the hydrogen sulfide in the scrubber is determined by sulfide SIE. A single lab evaluation was performed to determine the operating characteristics. The sulfide SIE is linear over the range 0.25-6000 mg/L sulfide with a detection limit of about 0.2 mg/L sulfide. Over the range 5-6000 mg/L, the relative precision of the SIE is 2-4 percent. The accuracy (expressed as percent recovery) over the range 0.25-6000 mg/L varies from 75-103 percent. The sulfide SIE is very selective for the sulfide dianion and in the scrubber solution, there are no interferences. Recoveries in real samples spiked with 17.5 mg/L sulfide varied from 68-77 percent before distillation and 93-98 percent after distillation. The results from the evaluation indicate that the sulfide SIE provides an alternate technique to determine sulfide in environmental samples after distillation.

This Project Summary was developed by EPA's Environmental Monitoring Sytems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Modifications to Methods 9030 and 9031 from "Test Methods for Evaluating Solid Waste (SW-846)" currently specified for the determination of sulfide have been developed that allow the use of sulfide specific ion electrodes (SIE). Currently, both methods require that sulfide be converted to hydrogen sulfide and distilled into a scrubber solution for subsequent determination by iodometric titration. In these proposed modifications, the hydrogen sulfide in the scrubber is determined by sulfide SIE. A single-lab evaluation was performed to determine the operating characteristics and performance of the draft methods. Data were collected on electrode linearity, precision, and accuracy. The effect of interferences and the possibility of direct measurement of sulfide without distillation were investigated. Finally, the recovery of hydrogen sulfide in the system was measured as a means to establish method accurracy. Electrode linearity was determined by measuring the sulfide concentration in 12 samples (ranging from 0.1 to 10,000 mg/L sulfide) and by comparing those values with values obtained using iodometric titration. Linear regression analysis indicates a linear range of 1 mg/L to 12,000 mg/L. The electrode response time was less than one minute over the linear concentration range; the detection limit was 0.2 mg/L.

Precision and accuracy were determined by measurement of three sulfide solutions that contained sulfide at a concentration greater than 10 times the detection limit. The relative precision was 2-4 percent and the accuracy (expressed as percent recovery) over the same range varied from 75 to 103 percent.

Compounds that interfere with the titration analysis of sulfide were tested as potential interference with the sulfide electrode analysis. Sodium sulfite and sodium thiosulfate, each at the 100 mg/L level, gave no significant SIE response.

There may be substances that can interfere with the chemistry of the sulfide SIE in undistilled environmental samples. According to the manufacturer, two potential interferences are silver ion and mercuric ion. Organic matter should not interfere with the electrode chemically, although there may be a physical effect due to coating of the electrode membrane. Humic acid (100 mg/L), mercuric ion (10 µg/L), and silver ion (20 mg/L) solutions were analyzed using the sulfide SIE, and each gave less than a 1 mg/L response for sulfide.

The direct measurement of sulfide in environmental samples was attempted by sulfide SIE. Four environmental samples (three soils and one waste oil) were mixed with a sulfide anti-oxidant buffer (SAOB) and the free sulfide levels were determined by SIE; those results were compared with results obtained using Method 9030. The spike recoveries varied from 68 to 77 percent for the SIE method as compared to 93 to 98 percent using Method 9030. This suggests that some of the sulfide was complexed and was not detected by the SIE. Therefore, sulfide SIE should be used in conjunction with distillation to ensure that hydrogen sulfide gas is liberated from any complexes or solid sulfides in the sample.

Prior to the titration procedure of Method 9030 and 9031, hydrogen sulfide gas is distilled into a zinc acetate scrubber solution. The modified SIE protocols specify that hydrogen sulfide gas be distilled into a SAOB scrubber solution. To test the efficiency of the SAOB as a scrubber solution, three standards (1, 10, and 40 mg/L sulfide) were distilled into SAOB and the resulting sulfide concentrations were measured. The results are listed in Table 1. The one low recovery for the 40 mg/L standard is most likely due to incomplete sparging of oxygen from the system prior to distillation. Oxygen oxidizes sulfide and will cause low recoveries.

This single lab evaluation has demonstrationed that the sulfide SIE is a suitable alternative technique for measuring sulfide in distillate absorbing solutions. Use of the sulfide SIE could double the capacity of laboratories that currently use the iodometric titration to measure sulfide.

Table 1. Recovery of Hydrogen Sulfide Gas at Different Concentrations in SAOB Scrubber Solution

Concentration of Sulfide (mg/L)	*% Recovery*
1	*91.0*
	89.8
	86.7
10	*96.6*
	100
	96.0
40	*69.3*
	98.9
	89.2

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The complete report, entitled ""Modification of Method 9030 and 9031 for the Analysis of Sulfide by Specific Ion Electrode," (Order No. PB90-274 235/AS; Cost: $17.00, cost subject to change) will be available only from:
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