

Quality Control

1. Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of replicate and spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within precision and accuracy limits expected of the method.

2. Before performing any analyses, the analyst must demonstrate the ability to generate acceptable precision and accuracy with this method by performing the following operations.

(a) Perform four replicate analyses of a 20 mg./l. sulfide standard prepared in distilled water (see paragraph 6 under "Reagents" above).

(b)(1) Calculate clean water precision and accuracy in accordance with standard statistical procedures. Clean water acceptance limits are presented in paragraph 2(b)(2) below. These criteria must be met or exceeded before sample analyses can be initiated. A clean water standard must be analyzed with each sample set and the established criteria met for the analysis to be considered under control.

(2) Clean water precision and accuracy acceptance limits: For distilled water samples containing from 5 mg./l. to 50 mg./l. sulfide, the mean concentration from four replicate analyses must be within the range of 50 to 110 percent of the true value.

3. The Method Detection Limits (MDL) should be determined periodically by each participating laboratory in accordance with the procedures specified in "Methods for Chemical Analysis of Municipal and Industrial Wastewater," EPA-660/4-82-057, July 1982, EMSL, Cincinnati, OH 45268. For the convenience of the user, these procedures are contained in appendix C to part 425.

4. A minimum of one spiked and one duplicate sample must be performed for each ana-

lytical event, or five percent spikes and five percent duplicates when the number of samples per event exceeds twenty. Spike levels are to be at the MDL (see paragraph 3 above for MDL samples) and at x where x is the concentration found if in excess of the MDL. Spike recovery must be 40 to 120 percent for the analysis of a particular matrix type to be considered valid. If a sample or matrix type provides performance outside these acceptance limits, the analyses must be repeated using the modified Monier-Williams procedures described in appendix B to this part.

5. Report results in mg./liter. When duplicate and spiked samples are analyzed, report all data with the sample results.

[53 FR 9183, Mar. 21, 1988]

APPENDIX B TO PART 425—MODIFIED
MONIER-WILLIAMS METHOD

Outline of Method

Hydrogen sulfide is liberated from an acidified sample by distillation and purging with nitrogen gas (N_2). Sulfur dioxide interference is removed by scrubbing the nitrogen gas stream in a pH 7 buffer solution. The sulfide gas is collected by passage through an alkaline hydrogen peroxide scrubbing solution in which it is oxidized to sulfate. Sulfate concentration in the scrubbing solution is determined by either EPA gravimetric test procedure 375.3 or EPA turbidimetric test procedure 375.4 (see 40 CFR 136.3, Table IB, parameter 65 (49 FR 43234, October 26, 1984, and correction notice at 50 FR 690, January 4, 1985)).

*Apparatus**

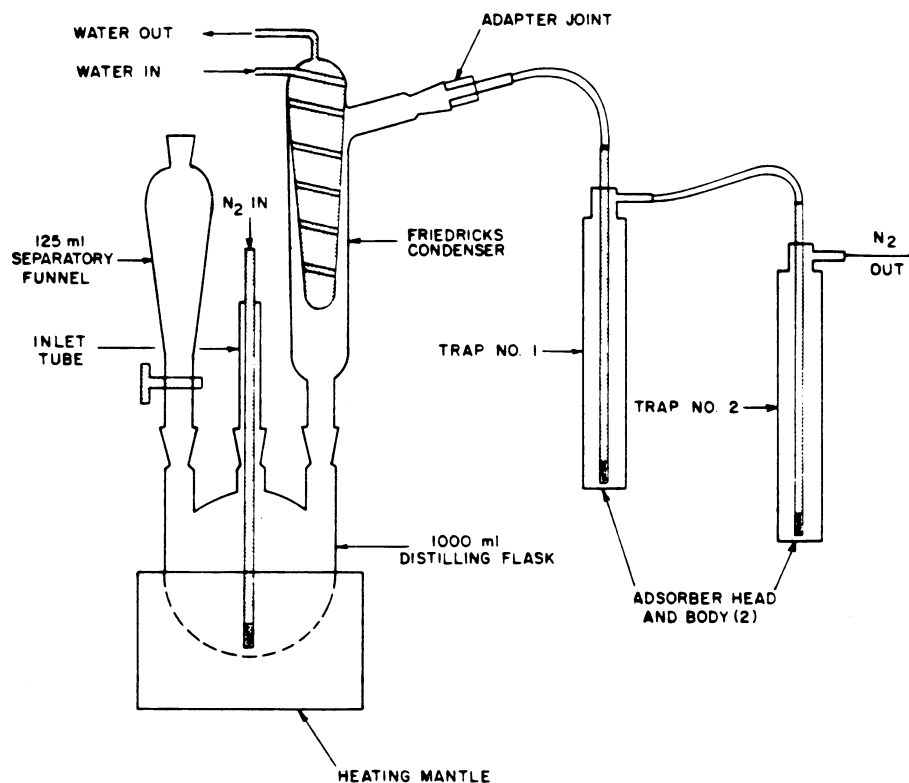
(See Figure 1.) * Catalogue numbers are given only to provide a more complete description of the equipment necessary, and do not constitute a manufacturer or vendor endorsement.

Heating mantle and control (VWR Cat. No. 33752-464)

1000 ml. distilling flask with three 24/40 joints (VWR Cat. No. 29280-215)

Friedricks condenser with two 24/40 joints (VWR Cat. No. 23161-009)

FIGURE 1
EQUIPMENT ASSEMBLY



125 ml. separatory funnel with 24/40 joint (VWR Cat. No. 30357-102)
 Inlet tube with 24/40 joint (VWR Cat. No. 33057-105)
 Adapter joint 24/40 to 19/38 (VWR Cat. No. 62905-26)
 Adsorber head (2 required) (Thomas Cat. No. 9849-R29)
 Adsorber body (2 required) (Thomas Cat. No. 9849-R32)
 Laboratory vacuum pump or water aspirator

Reagents

1. Potassium hydroxide, 6N: Dissolve 340 g. of analytical reagent grade KOH in 1 liter distilled water.
 2. Sodium hydroxide, 6N: Dissolve 240 g. of analytical reagent grade NaOH in 1 liter distilled water.

3. Sodium hydroxide, 0.03N: Dilute 5.0 ml. of 6N NaOH to 1 liter with distilled water.

4. Hydrochloric acid, 6N: Dilute 500 ml. of concentrated HCl to 1 liter with distilled water.

5. Potassium phosphate stock buffer, 0.5M: Dissolve 70 g. of monobasic potassium phosphate in approximately 800 ml. distilled water. Adjust pH to 7.0 ± 0.1 with 6N potassium hydroxide and dilute to 1 liter with distilled water. Stock solution is stable for several months at 4 °C.

6. Potassium phosphate buffer, 0.05M: Dilute 1 volume of 0.5M potassium phosphate stock buffer with 9 volumes of distilled water. Solution is stable for one month at 4 °C.

7. Alkaline 3% hydrogen peroxide: Dilute 1 volume of 30 percent hydrogen peroxide with

9 volumes of 0.03N NaOH. Prepare this solution fresh each day of use.

8. Preparation of stock sulfide standard, 1000 ppm.: Dissolve 2.4 g. reagent grade sodium sulfide in 1 liter of distilled water. Store in a tightly stoppered container. Diluted working standards must be prepared fresh daily and their concentrations determined by EPA test procedure 376.1 immediately prior to use (see 40 CFR 136.3, Table IB, parameter 66 (49 FR 43234, October 26, 1984, and correction notice at 50 FR 690, January 4, 1985)).

Sample Preservation and Storage

Preserve unfiltered wastewater samples immediately after collection by adjustment to pH>9 with 6N NaOH and addition of 2 ml. of 2N zinc acetate per liter. This amount of zinc acetate is adequate to preserve 64 mg./l. sulfide under ideal conditions. Sample containers must be covered tightly and stored at 4 °C until analysis. Samples must be analyzed within seven days of collection. If these procedures cannot be achieved, it is the laboratory's responsibility to institute quality control procedures that will provide documentation of sample integrity.

Procedure (See Figure 1 for apparatus layout.)

1. Place 50 ml. of 0.05M pH 7.0 potassium phosphate buffer in Trap No. 1.
2. Place 50 ml. of alkaline 3 percent hydrogen peroxide in Trap No. 2.
3. Sample introduction and N₂ prepurge: Gently mix sample to be analyzed to resuspend settled material, taking care not to aerate the sample. Transfer 400 ml. of sample, or a suitable portion containing not more than 20 mg. sulfide diluted to 400 ml. with distilled water, to the distillation flask. Adjust the N₂ flow so that the impingers are

frothing vigorously, but not overflowing. Vacuum may be applied at the outlet of Trap No. 2 to assist in smooth purging. The N₂ inlet tube of the distillation flask must be submerged deeply in the sample to ensure efficient agitation. Purge the sample for 30 minutes without applying heat. Test the apparatus for leaks during the prepurge cycle (Snoop or soap water solution).

4. Volatilization of H₂ S: Interrupt the N₂ flow (and vacuum) and introduce 100 ml. of 6N HCl to the sample using the separatory funnel. Immediately resume the gas flow (and vacuum). Apply maximum heat with the heating mantle until the sample begins to boil, then reduce heat and maintain gentle boiling and N₂ flow for 30 minutes. Terminate the distillation cycle by turning off the heating mantle and maintaining N₂ flow through the system for 5 to 10 minutes. Then turn off the N₂ flow (and release vacuum) and *cautiously* vent the system by placing 50 to 100 ml. of distilled water in the separatory funnel and opening the stopcock carefully. When the bubbling stops and the system is equalized to atmospheric pressure, remove the separatory funnel. Extreme care must be exercised in terminating the distillation cycle to avoid flash-over, draw-back, or violent steam release.

5. Analysis: Analyze the contents of Trap No. 2 for sulfate according to either EPA gravimetric test procedure 375.3 or EPA turbidimetric test procedure 375.4 (see 40 CFR 136.3, Table IB, parameter 65 (49 FR 43234, October 26, 1984, and correction notice at 50 FR 690, January 4, 1985)). Use the result to calculate mg./l. of sulfide in wastewater sample.

Calculations and Reporting of Results

1. Gravimetric procedure:

$$\text{mg sulfide/l.} = \frac{(\text{mg. BaSO}_4 \text{ collected in Trap No. 2}) \times (137)}{\text{volume in ml. of waste sample distilled}}$$

2. Turbidimetric procedure:

$$\text{mg. sulfide/l.} = \frac{A \times B \times 333}{C}$$

where A=mg./l. of sulfate in Trap No. 2
B=liquid volume in liters in Trap No. 2
and C=volume in ml. of waste sample distilled

3. Report results to two significant figures.

Quality Control

1. Each laboratory that uses this method is required to operate a formal quality control

program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of replicate and spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated. Ongoing performance checks must be compared with established performance criteria to determine if the results of analyses are within precision and accuracy limits expected of the method.

2. Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision by performing the following operations.

(a) Perform four replicate analyses of a 20 mg./l. sulfide standard prepared in distilled water (see paragraph 8 under "Reagents" above).

(b)(1) Calculate clean water precision and accuracy in accordance with standard statistical procedures. Clean water acceptance limits are presented in paragraph 2(b)(2) below. These criteria must be met or exceeded before sample analyses can be initiated. A clean water standard must be analyzed with each sample set and the established criteria met for the analyses to be considered under control.

(2) Clean water precision and accuracy acceptance limits: For distilled water samples containing from 5 mg./l. to 50 mg./l. sulfide, the mean concentration from four replicate analyses must be within the range of 72 to 114 percent of the true value.

3. The Method Detection Limit (MDL) should be determined periodically by each participating laboratory in accordance with the procedures specified in "Methods for Chemical Analysis of Municipal and Industrial Wastewater," EPA-600/4-82-057, July 1982, EMSL, Cincinnati, OH 45268. For the convenience of the user, these procedures are contained in appendix C to part 425.

4. A minimum of one spiked and one duplicate sample must be run for each analytical event, or five percent spikes and five percent duplicates when the number of samples per event exceeds twenty. Spike levels are to be at the MDL (see paragraph 3 above for MDL samples) and at x when x is the concentration found if in excess of the MDL. Spike recovery must be 60 to 120 percent for the analysis of a particular matrix type to be considered valid.

5. Report all results in mg./liter. When duplicate and spiked samples are analyzed, report all data with the sample results.

[53 FR 9184, Mar. 21, 1988]

APPENDIX C TO PART 425—DEFINITION AND PROCEDURE FOR THE DETERMINATION OF THE METHOD DETECTION LIMIT¹

The method detection limit (MDL) is defined at the minimum concentration of a substance that can be identified, measured and reported with 99 percent confidence that the analyte concentration is greater than

zero and determined from analysis of a sample in a given matrix containing analyte.

Scope and Application

This procedure is designed for applicability to a wide variety of sample types ranging from reagent (blank) water containing analyte to wastewater containing analyte. The MDL for an analytical procedure may vary as a function of sample type. The procedure requires a complete, specific and well defined analytical method. It is essential that all sample processing steps of the analytical method be included in the determination of the method detection limit.

The MDL obtained by this procedure is used to judge the significance of a single measurement of a future sample.

The MDL procedure was designed for applicability to a broad variety of physical and chemical methods. To accomplish this, the procedure was made device- or instrument-independent.

Procedure

1. Make an estimate of the detection limit using one of the following:

(a) The concentration value that corresponds to an instrument signal/noise ratio in the range of 2.5 to 5. If the criteria for qualitative identification of the analyte is based upon pattern recognition techniques, the least abundant signal necessary to achieve identification must be considered in making the estimate.

(b) The concentration value that corresponds to three times the standard deviation of replicate instrumental measurements for the analyte in reagent water.

(c) The concentration value that corresponds to the region of the standard curve where there is a significant change in sensitivity at low analyte concentrations, *i.e.*, a break in the slope of the standard curve.

(d) The concentration value that corresponds to known instrumental limitations.

It is recognized that the experience of the analyst is important to this process. However, the analyst must include the above considerations in the estimate of the detection limit.

2. Prepare reagent (blank) water that is as free of analyte as possible. Reagent or interference free water is defined as a water sample in which analyte and interferent concentrations are not detected at the method detection limit of each analyte of interest. Interferences are defined as systematic errors in the measured analytical signal of an established procedure caused by the presence of interfering species (interferent). The interferent concentration is presupposed to be normally distributed in representative samples of a given matrix.

3. (a) If the MDL is to be determined in reagent water (blank), prepare a laboratory

¹Source: "Methods for Chemical Analysis of Municipal and Industrial Wastewater," EPA-600/4-82-057, July 1982, EMSL, Cincinnati, OH 45268