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MODIFICATION OF METHODS 9030 AND 9031 FOR THE ANALYSIS OF SULFIDE BY SPECIFIC ION ELECTRODE

by

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ABSTRACT

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 is 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 response time for the electrode was less than a minute over the entire linear concentration range. The sulfide SIE is very selective for the sulfide dianion, and in the scrubber solution, there are no interferences. If the sulfide SIE is used to measure sulfide directly in samples (i.e., no distillation), mercury and silver ions may interfere. However, under the conditions of analysis (pH>12), neither ion is present at interfering concentrations. Another factor is important if the SIE is used to determine sulfide directly; it only responds to free sulfide dianion and will not detect sulfide tied up in complexes. 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.

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INTRODUCTION

Currently two methods for determining sulfide exist in OSW SW-846 "Test Methods for Evaluating Solid Waste", Method 9030 and Method 9031. Method 9030 is useful for determining acid-soluble and acid-insoluble sulfide in aqueous and solid waste materials and effluents except those which contain oil, are multiphasic, or are not amenable to distillation. Method 9031 is useful for determining extractable sulfide and essentially is applicable to all samples which can't be analyzed by Method 9030.

In Method 9030, samples are acidified to convert all free sulfide and acid-soluble sulfides to H_2S, which is distilled into a zinc acetate scrubber solution. Sulfide in the scrubber is then determined by iodometric titration. Acid-insoluble sulfide is determined similarly except that the acidification/ distillation step is more severe. In Method 9031, sulfides are extracted from oily or non-aqueous phases into a basic aqueous phase. Any original aqueous phase and the basic extract are then combined, acidified, and the sulfide distilled into a zinc acetate scrubber solution. Sulfide in the scrubber is then determined by iodometric titration.

In both Method 9030 and 9031, the distillation step is inherent in the method. However, once distilled, methods other than iodometric titration exist for the determination of sulfide in the scrubber. One alternative method is the sulfide SIE. The sulfide SIE in general is very sensitive and interference-free. The most common interfering ions are silver and mercury, neither of which will be present in the distillate scrubber. This is an advantage over the titrimetric method, which suffers from interferences due to other sulfur compounds (sulfite, thiosulfate, sulfur dioxide) which can distill over into the scrubber.

The purpose of this study was to evaluate the use of the sulfide SIE to measure sulfide in the distillate scrubber. The distillate scrubber in Methods 9030 and 9031 is a zinc acetate solution in which the distilled sulfide is precipitated as zinc sulfide. To use the SIE, the scrubber is changed to sulfide anti-oxidant buffer (SAOB, a sodium hydroxide solution (pH>12) with ascorbic and salicylic acids added as an oxygen scavengers). The precision, accuracy, and linearity of the sulfide SIE were determined in the scrubber matrix as well as the response time of the electrode and its ease of operation.

Effects of known interferences (silver ion and mercuric ion) in undistilled samples were evaluated. Also the use of the SIE for the direct measurement of sulfide in environmental samples was demonstrated. Both spiked and unspiked samples were measured. The direct measurements were compared to results obtained by Method 9030. Based on this evaluation, protocols for Method 9030 and Method 9031 were modified to include the use of the sulfide SIE. The modified protocols are attached as Appendix A and B, respectively.

EXPERIMENTAL DESIGN

EXPERIMENT 1 (LINEARITY)

The sulfide SIE was calibrated with 100 and 1000 mg/L standards. Twelve sulfide samples were prepared (0.1, 0.25, 0.5, 1, 5, 25, 50, 100, 500, 1,000, 5,000, 10,000 mg/L sulfide). The samples were analyzed in a random order (25, 1,000, 0.5, 10,000, 500, 0.25, 1, 100, 0.1, 5, 50, 5,000). The three low and three high samples were analyzed in triplicate. The measured concentration was plotted vs. true concentration and a linear regression was calculated.

EXPERIMENT 2 (PRECISION AND ACCURACY)

Three sulfide samples were prepared (low, medium, and high; 25, 100, and 1000 mg/L). Triplicate measurements of each were performed in the following order; medium, low, high, high, low, medium. Precision estimates were calculated from the average percent RSD taken within each block of triplicate measurements. Accuracy estimates were calculated from average percent recovery.

EXPERIMENT 3 (INTERFERENCES)

No interferences were expected in the scrubber solution. However the compounds that interfere with the titration analysis were tested for interference with the sulfide electrode analysis. Portions of a 100 mg/L sulfide sample were spiked TO contain 100 mg/L sodium sulfite and 100 mg/L sodium thiosulfate. An unspiked sample and the two spiked samples were analyzed to check for any interference.

In environmental samples (undistilled), there are few substances which can interfere with the chemistry of the sulfide SIE. The two major interferences are silver ion and mercuric ion. Organic species will not interfere chemically with the electrode, though they can cause physical interferences (i.e., by coating the electrode). An experiment was performed to test the effect of silver and mercury on the sulfide SIE. Silver was also tested with the addition of ammonia, which prevents silver precipitation in the basic measuring solution. Additionally, the effect of humic acid, a common natural organic compound, was also studied. In this experiment, two matrices were studied; deionized water and tap water. The experimental procedure entailed the following steps: Mix 8 mL of the SAOB and 25 mL of the matrix containing the interferent, filter the solution, measure sulfide by SIE.

EXPERIMENT 4 (DIRECT MEASUREMENT IN REAL SAMPLES)

The sulfide SIE responds only to dissolved sulfide ion. Any sulfide present as a solid or complex was not detected by the sulfide SIE. Four samples (described below) were prepared by slurrying the sample with SAOB and measuring sulfide with the SIE. The experiment was repeated after spiking the sample with sulfide. The experiment was repeated for the spiked samples using Method 9030 to determine sulfide.

Sample	Description
Sand	100% silica sand
Soil 1	soil contaminated with heavy metals
Soil 2	soil contaminated with heavy metals
Oil	NIST base oil 1083

EXPERIMENT 5 (RECOVERY OF DISTILLED HYDROGEN SULFIDE IN THE SAOB SCRUBBER)

As part of Methods 9030 and 9031, hydrogen sulfide gas was distilled from a sample and absorbed into a zinc acetate scrubber solution. For the modified protocols using the sulfide SIE, the hydrogen sulfide gas was distilled from a sample and absorbed 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 scrubber and the resulting sulfide concentration measured.

PROCEDURE

APPARATUS

Orion Silver/Sulfide Electrode, Model 94-16

Orion Double Junction Reference Electrode, Model 90-20-00

Orion Ion Analyzer 940

REAGENTS

Sulfide Stock Solution (10,000 mg/L)

Dissolve 24.3 g anhydrous Na_2S (or 74.7 g $Na_2S \cdot 9H_2O$) and 10 g NaOH in 1 L reagent water. Keep tightly closed and store at 4°C. Standardize weekly by iodometric titration.

Sulfide Stock Solution (1,000 mg/L)

Dissolve 2.4 g anhydrous Na_2S (or 7.5 g $Na_2S \cdot 9H_2O$) and 10 g NaOH in 1 L reagent water. Keep tightly closed and store at 4°C. Standardize weekly by iodometric titration.

Dilute Sulfide Solutions

The following dilute sulfide solutions must be prepared daily as required.

5,000 mg/L - Pipet 20.00 mL scrubber solution and 50.00 mL 10,000 mg/L sulfide stock solution into a 100 mL volumetric flask and dilute to the mark with reagent water.

500 mg/L - Pipet 20.00 mL scrubber solution and 50.00 mL 1,000 mg/L sulfide stock solution into a 100 mL volumetric flask and dilute to the mark with reagent water.

100 mg/L - Pipet 20.00 mL scrubber solution and 10.00 mL 1,000 mg/L sulfide stock solution into a 100 mL volumetric flask and dilute to the mark with reagent water.

50 mg/L - Pipet 20.00 mL scrubber solution and 5.00 mL 1,000 mg/L sulfide stock solution into a 100 mL volumetric flask and dilute to the mark with reagent water.

25 mg/L - Pipet 20.00 mL scrubber solution and 2.50 mL 1,000 mg/L sulfide stock solution into a 100 mL volumetric flask and dilute to the mark with reagent water.

5 mg/L - Pipet 20.00 mL scrubber solution and 0.500 mL 1,000 mg/L sulfide stock solution into a 100 mL volumetric flask and dilute to the mark with reagent water.

1 mg/L - Pipet 20.00 mL scrubber solution and 0.100 mL 1,000 mg/L sulfide stock solution into a 100 mL volumetric flask and dilute to the mark with reagent water.

0.5 mg/L - Pipet 20.00 mL scrubber solution and 0.0500 mL 1,000 mg/L sulfide stock solution into a 100 mL volumetric flask and dilute to the mark with reagent water.

0.25 mg/L - Pipet 20.00 mL scrubber solution and 0.0250 mL 1,000 mg/L sulfide stock solution into a 100 mL volumetric flask and dilute to the mark with reagent water.

0.1 mg/L - Pipet 20.00 mL scrubber solution and 0.0100 mL 1,000 mg/L sulfide stock solution into a 100 mL volumetric flask and dilute to the mark with reagent water.

Zinc Acetate Solution (2 N)

Dissolve 220 g zinc acetate dihydrate $Zn(CH_3COO)_2 \cdot 2H_2O$ in 500 mL reagent water then dilute to 1,000 mL.

Starch Indicator Solution

Dissolve 2 g laboratory grade soluble starch and 0.2 g salicylic acid (as a preservative) in 100 mL hot reagent water.

Iodine Solution (0.025 N)

Dissolve 20-25 g KI in 200 mL reagent water. Add 3.2 g iodine then dilute to 1,000 mL. Standardize with 0.025 N $Na_2S_2O_3$ using a starch indicator.

Thiosulfate Solution (0.025 N)

Dissolve 6.205 g $Na_2S_2O_3 \cdot 5H_2O$ in reagent water. Add 1.5 mL 6 N NaOH (or 0.4 g solid NaOH) and dilute to 1,000 mL. Standardize with potassium iodate solution.

Potassium Iodate Solution (0.0490 N)

Dissolve 0.1748 g primary standard grade KIO_3 (dried at 105°C for 1 hour) in reagent water and dilute to 100 mL in a volumetric flask.

Sodium Hydroxide Solution (6 N)

Dissolve 240 g NaOH in 1,000 mL reagent water. Keep tightly closed.

Sulfide Anti-Oxidant Buffer (SAOB)

Dissolve 80 g NaOH, 320 g sodium salicylate, and 72 g ascorbic acid in 1 L reagent water. Prepare fresh weekly.

Reagent Water

Water used to prepare reagents and standards must conform to ASTM specifications for Type II water (ASTM, 1984, Vol.11.01, D1193-77).

REAGENT STANDARDIZATION

Stock Sulfide Solutions

Dilute 5.00 mL standard sulfide solution to 100 mL with reagent water. Add 5.00 mL 0.025 N iodine solution and 2.0 mL 6 N HCl. Back titrate with 0.025 N $Na_2S_2O_3$ solution, adding a few drops of starch indicator as end point is approached. Continue titration until blue color disappears. The concentration is calculated as follows;

$$Sulfide\ (mg/L) = \frac{[(A \times B) - (C \times D)] \times 16000}{E}$$

A = volume of iodine solution (5.00 mL)
B = normality of iodine
C = volume of $Na_2S_2O_3$ solution (mL)
D = normality of $Na_2S_2O_3$ solution (eq/L)
E = volume of sulfide standard (5.00 mL)

Thiosulfate Solution

Dissolve 2 g KI (free from iodate) in 100 mL reagent water. Add 2 mL 6 N HCl and 5.00 mL iodate solution. Dilute to 200 mL and titrate the liberated iodine with the thiosulfate solution, adding starch indicator as the endpoint is approached (pale straw color). The endpoint is reached when the solution changes from dark blue to colorless. Calculate the thiosulfate concentration as follows;

$$Thiosulfate\ conc.\ (eq/L) = \frac{A \times B}{V}$$

A = volume of iodate solution (5.00 mL)
B = normality of iodate solution (eq/L)
V = volume of thiosulfate solution (mL)

Iodine Solution

Dilute 5.00 mL of iodine solution to 100 mL with reagent water. Titrate with the standardized thiosulfate solution, add 2 mL of starch indicator as the endpoint is approached. Continue titration to the endpoint. Calculate the iodine solution concentration as follows;

$$Iodine\ conc.\ (eq/L) = \frac{V \times C}{A}$$

V = volume of thiosulfate solution (mL)
A = volume of iodine solution (5.00 mL)
C = thiosulfate normality (eq/L)

SULFIDE ELECTRODE ANALYSIS

Calibration of the Ion meter

The ion meter was calibrated following the manufacturer's directions using 1,000 and 100 mg/L sulfide standards.

Sample Analysis

The following procedure was used to analyze samples using the sulfide electrode.

1) Rinse the electrodes thoroughly with reagent water.
2) Add 60 mL sample and 20 mL SAOB to a disposable beaker and cover with a polyethylene lid.
3) Place on insulated stir plate and begin stirring.
4) Insert the electrodes. Record the sulfide concentration and analysis time when a stable reading is obtained.

RESULTS AND DISCUSSION

EXPERIMENT 1 (LINEARITY)

The sulfide SIE was connected to a ion meter and a series of sulfide standards analyzed (Table 1). The electrode response vs. the log of the sulfide concentration is plotted in Figure 1. The curve is linear over the range 1-12,000 mg/L. For practical routine analysis, the sulfide SIE is calibrated using a 2-point calibration. To evaluate practical analyses, the sulfide SIE was calibrated with 100 and 1000 mg/L standards, the a series of standards analyzed as unknowns. The results are listed in Table 2. Recoveries ranged from 76-124% over the range 0.25-12,000 mg/L sulfide. This indicates that there is no practical difference between the true and observed values for sulfide over this concentration range. The detection limit is estimated to be about 0.2 mg/L sulfide (from the precision at the 0.5 mg/L level).

TABLE 1. SULFIDE SIE RESPONSE VS. SULFIDE CONCENTRATION

SULFIDE (mg/L)	RESPONSE (mV)
0.100	-767.8
0.250	-769.1
0.500	-770.7
0.500	-771.1
1.000	-774.1
1.09	-774.6
5.00	-786.2
27.4	-805.5
55.0	-813.7
110	-821.8
591	-843.7
1183	-852.3
6000	-873.8
12000	-885.6

TABLE 2. COMPARISON OF TRUE SULFIDE CONCENTRATION VS. CONCENTRATION MEASURED BY SULFIDE SIE

True (mg/L)	Measured (mg/L)	Std. Dev (mg/L)	RSD (%)	Recovery (%)
0	-0.2			
0.10	0.01			10
0.25	0.19			76
0.50	0.47	0.059	12.7	94
1.00	0.99	0.092	9.3	99
1.09	1.10			101
5.00	4.94	0.17	3.4	99
27.4	26.8			98
55.0	52.3			95
110	109			99
591	607			103
1183	1157	5.2	0.4	98
6000	6028	123	2.0	100
12000	14850	332	2.2	124
n = 3 for samples with standard deviation				

EXPERIMENT 2 (PRECISION AND ACCURACY)

After calibration, the sulfide SIE was used to measure the concentration of three standards six times each. The data is listed in Table 3. Upon examination of the data in Tables 2 and 3, it is apparent that for sulfide concentrations greater than 10 times the detection limit (estimated at 0.2 mg/L), the relative precision ranges from 2-4 percent. Over the entire range, 0.25-12,000 mg/L, the percent recovery ranges from 75-124 percent.

TABLE 3. PRECISION AND ACCURACY DATA FOR THE SULFIDE SIE

True (mg/L)	Measured (mg/L)	Std. Dev. (mg/L)	RSD (%)	Recovery (%)
23.6	19.2	0.81	4.2	82.5
118.1	114.8	2.2	1.9	97.2
1503	1455	26	1.8	96.8
n = 6 for all samples				

EXPERIMENT 3 (INTERFERENCES)

The effect of sulfur compounds (with sulfur in the +4 oxidation state) on the sulfide SIE in the absorbing solution (which interfere with the titrimetric method) was tested (e.g., sulfite or

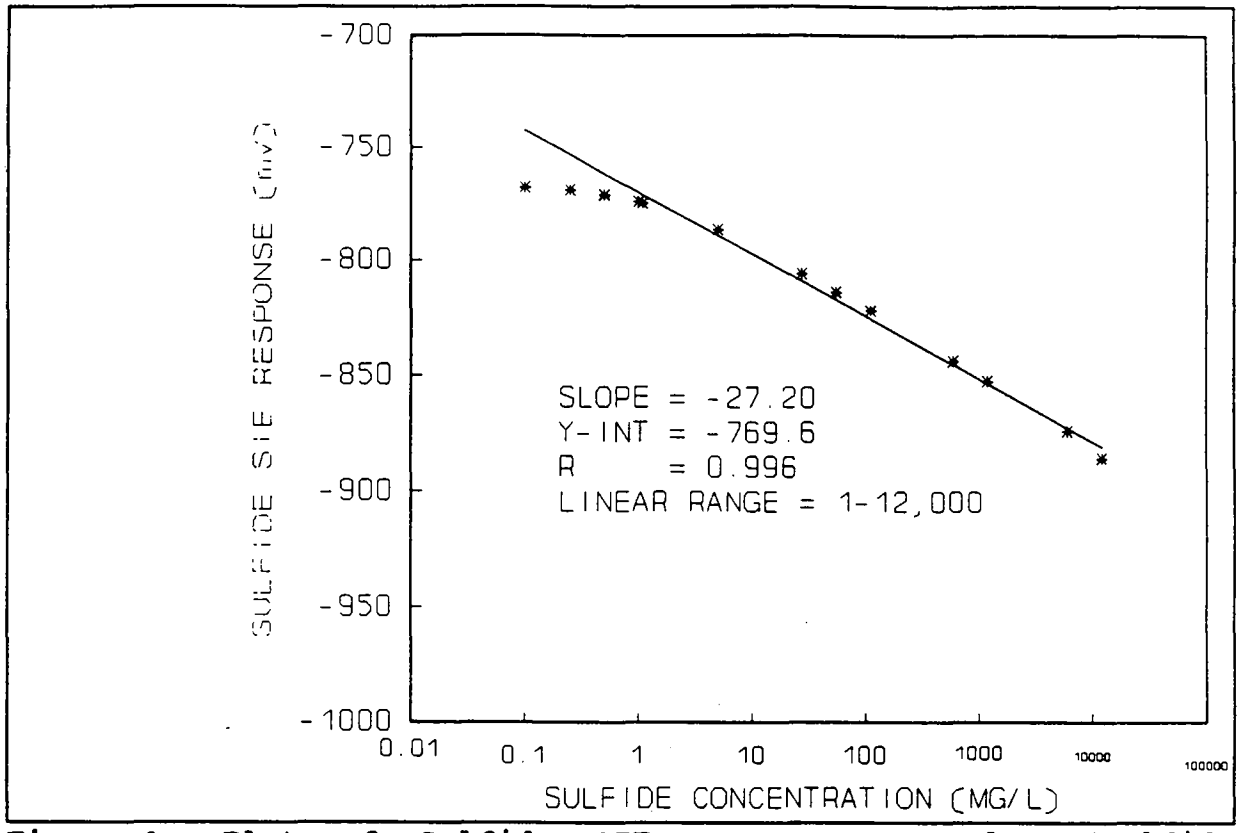

Figure 1. Plot of Sulfide SIE response vs. log (sulfide concentration, mg/L)

thiosulfate). The electrode did not respond to either compound. A 110 mg/L sulfide solution was spiked with 100 mg/L sulfite and 100 mg/L thiosulfate. The measured concentrations for the unspiked and spiked samples were identical (114 mg/L).

The effects of silver, mercury, and humic acid on the sulfide SIE are presented in Table 4.

TABLE 4. INTERFERENCE STUDY RESULTS

Interferent	Sulfide Concentration (mg/L)	
	DI matrix	Tap water matrix
Ag^+ (20 mg/L)	<1	<1
$Ag^+ + NH_4^+$ (20 mg/L each)	<1	<1
Hg^+ (20 mg/L)	<1	<1
Humic acid (100 mg/L)	2.1	1.6
Humic acid + sulfide (100 mg/L each)	114	87.8
* The humic acid contains 2-3 mg/L sulfide as determined by Method 9030.		

The data indicates that neither silver, mercury, nor humic acid interfere with the electrode. An interference would be indicated by a positive response. This is not surprising for the conditions of analysis, which are at pH>12. At this pH, both silver and mercury precipitate and do not effect the electrode. If ammonia is present, silver still does not interfere. Apparently the silver-ammonia complex prevents any silver present from interfering with the electrode. Silver and mercury are listed as interferents (by the electrode manufacturers) for the sulfide electrode for analyses performed under different conditions (i.e. those in which the ions are in solution).

SULFIDE SIE OPERATING CHARACTERISTICS

The response time of the electrode was less than 1 minute across the entire concentration range investigated. The stability of the electrode is affected by the solution temperature. A change in temperature of 1°C results in a 4% error (Orion Model 94-16 Silver/Sulfide Electrode Manual). Most ion meters have the capability of empirically correcting for temperature drift throughout the course of a day. However, for the most accurate and precise work, samples and standards should all be equilibrated to the same temperature.

SULFIDE STANDARDS

Sulfide standards are subject to degradation due to oxidation by dissolved oxygen. However, when prepared fresh daily in SAOB, the sulfide standards are stable throughout a working day (less than 10% degradation over 6-8 hours). Standardization of the sulfide standards is a critical step in calibrating the sulfide SIE. The calibration standards must be independently standardized daily. Standardization is normally performed by iodometric titration. The iodometric titration is tedious and labor intensive; a solution of thiosulfate is standardized against a standard iodate solution, an iodine solution is standardized against the thiosulfate solution, and the sulfide standard is standardized against the iodine solution/thiosulfate solution. Also the iodine solution requires daily calibration itself. An alternate procedure for standardizing the sulfide calibration standards is by a potentiometric titration with standardized silver nitrate using the sulfide SIE as the working electrode. Silver nitrate solutions are stable when stored properly and are easily standardized against sodium chloride.

DIRECT MEASUREMENT IN REAL SAMPLES

The sulfide SIE responds only to dissolved sulfide ion. Any sulfide present as a solid or complex will not be detected by the sulfide SIE. Four samples were prepared by slurring the sample with SAOB and measuring sulfide with the SIE. The experiment was repeated after spiking the sample with 17.5 mg/L sulfide. The experiment was repeated for the spiked samples using Method 9030 to determine sulfide. The results are presented in Table 5.

The spike recovery varies from 68-77 percent for the SIE results and from 93-98 percent for the Method 9030 results. This indicates that some of the added sulfide is tied up and not

TABLE 5. RESULTS FOR THE DIRECT COMPARISON OF SULFIDE BY SIE AND COMPARISON TO METHOD 9030

Sample	Spike added (mg/L)	Results			
		SIE		Method 9030	
		(mg/L)	% Recovery	(mg/L)	% Recovery
Sand	0	<3			
	17.5	12.5	71.4	16.6	94.9
Soil 1	0	<3			
	17.5	13.4	76.6	17.1	97.7
Soil 2	0	<3			
	17.5	11.7	66.9	16.3	93.1
Oil	0	<3			
	17.5	12.5	71.4	16.6	94.9

detected by the SIE, which is expected. Recoveries are better for Method 9030 because hydrogen sulfide gas is liberated from any complexed or solid sulfide during the distillation step.

RECOVERY OF DISTILLED HYDROGEN SULFIDE IN THE SAOB SCRUBBER

As part of Methods 9030 and 9031, hydrogen sulfide gas is distilled from a sample and absorbed into a zinc acetate scrubber solution. For the modified protocols using the sulfide SIE, the hydrogen sulfide gas is distilled from a sample and absorbed 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 scrubber and the resulting sulfide concentration measured. The results are listed in Table 6. As seen in the table, excellent recoveries are obtained using the SAOB scrubber solution. 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. The key to acceptable recoveries is the use of the proper apparatus and careful assembly of the distillation apparatus to prevent leaks in the flow path. Additionally it is important to sparge oxygen from the apparatus prior to distillation. If these steps are not taken, low recoveries will result, as seen in the initial trials performed to test the recovery in SAOB, in which results ranged from 20-95 percent.

TABLE 6. RECOVERY OF HYDROGEN SULFIDE IN SAOB SOLUTION

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

DISCUSSION AND CONCLUSIONS

The sulfide SIE can be used to quantitatively detect soluble, uncomplexed sulfides in both liquid and solid samples (after slurring with SAOB). However results may not be comparable to those obtained by Methods 9030 or 9031, which measure total sulfide. If solid or complexed sulfides are present, SIE results may be biased low. In such instances, the bias can be minimized by performing the distillation step in Method 9030 prior to analysis. Once distilled, sulfide can be analyzed acceptably by either titration or SIE. If measured by SIE, the distillation scrubber solution is replaced by SAOB.

The use of a sulfide SIE is a simple procedure to measure sulfide ion in distillates obtained from environmental samples. Distillation separates sulfide (as hydrogen sulfide gas) from any significant matrix interferences present in environmental matrices (water, soil, and oil sample matrices have been tested). Of course (as with all electrodes), if the electrode membrane becomes fouled or scratched, its performance will be affected and it will have to be cleaned or polished. The primary drawback with sulfide SIEs is the stability of calibration standards, which can degrade by more than 10% from day-to-day. Standards have to be standardized daily before use (by titration) and checked throughout the day if used as QC samples. For the determination of total sulfide, the sulfide SIE offers no marked advantages over the typical titration, as the distillation step is rate-limiting. If a better distillation procedure is developed (e.g., using the Lachat micro-block distillation apparatus), the ease of automating the measurement step will be a factor in determining which technique is better.

This evaluation has demonstrated that the sulfide SIE provides an alternate technique for quantifying sulfide in distillate absorbing solutions. The precision and accuracy of the sulfide SIE are adequate for sulfide determinations (2-4 percent RSD, 75-105 percent recoveries). Using the sulfide SIE should increase throughput by a factor of two when compared to the iodometric titration. Also, if the sulfide SIE is used, it is simpler to standardize the calibration standards with a potentiometric titration rather than the iodometric titration.

APPENDIX A

MODIFIED METHOD 9030

ACID-SOLUBLE AND ACID-INSOLUBLE SULFIDES

1.0 SCOPE AND APPLICATION

1.1 The distillation procedure described in this method is designed for the determination of sulfides in aqueous and solid waste materials and effluent.

1.2 This method provides only a semi-quantitative determination of sulfide compounds considered acid-insoluble (e.g. CuS and SnS_2) in solid samples. Recovery has been shown to be 20 to 40 percent for CuS, one of the most stable and insoluble compounds, and 40 to 60 percent for SnS_2 which is slightly more soluble.

1.3 This method is not applicable to oil or multiphasic samples or samples not amenable to the distillation procedure. These samples can be analyzed by Method 9031.

1.4 Method 9030 is suitable for measuring sulfide concentrations in samples which contain between 0.2 and 50 mg/kg of sulfide.

1.5 This method is not applicable for reactive sulfide. Refer to Chapter Seven, Step 7.3.4.1 for the determination of reactive sulfide.

1.6 This method measures total sulfide which is usually defined as the acid-soluble fraction of waste. If, however, one has previous knowledge of the waste and is concerned about both soluble sulfides such as H_2S, and metal sulfides, such as CuS and SnS_2, then total sulfide is defined as the combination of both acid-soluble and acid-insoluble fractions. For wastes where only metal sulfides are suspected to be present, only the acid-insoluble fraction needs to be measured.

2.0 SUMMARY OF METHOD

2.1 For acid-soluble samples, separation of sulfide from the sample matrix is accomplished by the addition of sulfuric acid to the sample. The sample is heated to 70°C and the hydrogen sulfide (H_2S) which is formed is distilled under acidic conditions and carried by a nitrogen stream into gas scrubbing bottles. If the sulfide is to be determined by titration, the gas scrubbers contain zinc acetate where sulfide is precipitated as zinc sulfide. If the sulfide is determined by sulfide ion specific electrode (SIE), the gas scrubbers contain sulfide anti-oxidant buffer (SAOB, a sodium hydroxide solution containing salicylic and ascorbic acids at a pH>12) where it is trapped as sulfide ion.

2.2 For acid-insoluble sulfide samples, separation from the sample matrix is accomplished by suspending the sample in concentrated hydrochloric acid by vigorous agitation. Tin(II) chloride is present to prevent oxidation of sulfide to sulfur by metal ions (e.g.,

copper(II)), by the matrix, or by dissolved oxygen in the reagents. The prepared sample is distilled under acidic conditions at 100°C under a stream of nitrogen. Hydrogen sulfide gas is released from the sample and collected in gas scrubbing bottles containing either a zinc acetate buffer or SAOB.

2.3 If determined by titration, the sulfide in the zinc sulfide precipitate is oxidized to sulfur with a known excess amount of iodine. The excess iodine is determined by titration with a standard solution of phenyl arsine oxide (PAO) or sodium thiosulfate until the blue iodine starch complex disappears. As the use of standard sulfide solutions is difficult because of oxidative degradation, quantitation is based on the PAO or sodium thiosulfate.

2.4 If determined by sulfide SIE, the sulfide in the SAOB is determined directly with a calibrated sulfide SIE. The sulfide SIE is calibrated using freshly standardized sulfide standards in a SAOB matrix (to minimize degradation prior to calibration). The sulfide standards are standardized by either a thiosulfate or silver nitrate titration.

3.0 INTERFERENCES

3.1 Aqueous samples must be taken with a minimum of aeration to avoid volatilization of sulfide or reaction with oxygen, which oxidizes sulfide to sulfur compounds that are not detected.

3.2 Reduced sulfur compounds, such as sulfite and hydrosulfite, decompose in acid, and may form sulfur dioxide. This gas may be carried over to the zinc acetate gas scrubbing bottles and subsequently react with the iodine solution yielding false high value. The addition of formaldehyde into the zinc acetate gas scrubbing bottles removes this interference. Any sulfur dioxide entering the scrubber will form an addition compound with the formaldehyde which is unreactive towards the iodine in the acidified mixture. This methods shows no sensitivity to sulfite or hydrosulfite at concentrations up to 10 mg/kg of the interferant. Sulfur dioxide will not interfere with the SIE determination.

3.3 Interferences for acid-insoluble sulfides have not been fully investigated. However, sodium sulfite and sodium thiosulfate are known to interfere in the procedure for soluble sulfides. Sulfur also interferes because it may be reduced to sulfide by tin(II) chloride in this procedure.

3.4 The iodometric method suffers interference from reducing substances that react with iodine, including thiosulfate, sulfite, and various organic compounds. The SIE method is free from interferences.

3.5 The insoluble method should not be used for the determination of soluble sulfides because it can reduce sulfur to sulfide, thus creating a positive interference.

4.0 APPARATUS AND MATERIALS

4.1 Distillation apparatus as shown in Figure 1.

4.1.1 Three Neck Flask--500 mL, 24/40 standard taper joints.

4.1.2 Dropping Funnel--100 mL, 24/40 outlet joint.

4.1.3 Purge Gas Inlet Tube--24/40 joint, with coarse frit.

4.1.4 Purge Gas Inlet Tube--24/40 joint, with coarse frit.

4.1.5 Gas Scrubbing Bottles--125 mL, with ¼ in. o.d. inlet and outlet tubes. Impinger tube must be fritted.

4.1.6 Tubing--¼ in. o.d. Teflon or polypropylene. Do not use rubber.

4.2 Sulfide SIE

4.3 Double Junction reference electrode

4.4 pH/mV/Ion meter capable of reading to 0.1 mV

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D-1193-77 (1983)) -- All water used in this method will be Type II unless otherwise specified.

5.3 Zinc Acetate Solution for Sample Preservation (2N) -- Dissolve 220 g of zinc acetate dihydrate in 500 mL of water.

5.4 Sodium Hydroxide (1N), NaOH -- Dissolve 40 g of NaOH in water and dilute to 1 liter.

5.5 Formaldehyde (37 percent solution) -- This solution is commercially available.

5.6 Zinc Acetate for the Scrubber

5.6.1 For Acid-Soluble Sulfides Zinc Acetate Solution (approximately 0.5M)--Dissolve about 110 g zinc acetate dihydrate in 200 mL of water. Add 1 mL hydrochloric acid (concentrated), HCl, to prevent precipitation of zinc hydroxide. Dilute to 1 liter.

5.6.2 For Acid-Insoluble Sulfides Zinc Acetate/Sodium Acetate Buffer -- Dissolve 100 g sodium acetate, and 11 g zinc acetate dihydrate in 800 mL of water. Add 1 mL concentrated hydrochloric acid and dilute to 1 liter. The resulting pH should be 6.8.

5.7 Acid to Acidify the Sample

5.7.1 For Acid-Soluble Sulfides -- Sulfuric acid (concentrated)

5.7.2 For Acid-Insoluble Sulfides -- Hydrochloric acid (9.8N). Place 200 mL of water in 1 liter beaker. Slowly add concentrated HCl to bring the total volume to 1 liter.

5.8 Starch Solution -- Use either an aqueous solution or soluble starch powder mixtures. Prepare an aqueous solution as follows. Dissolve 2 g soluble starch and 2 g salicylic acid, as a preservative, in 100 mL hot water.

5.9 Nitrogen gas

5.10 Iodine Solution (approximately 0.025N)--Dissolve 25 g potassium iodide, KI, in 700 mL of water in a 1 liter volumetric flask. Add 3.2 g iodine. Allow to dissolve. Dilute to 1 liter and standardize as follows. Dissolve approximately 2 g KI in 150 mL of water. Pipet exactly 20 mL of the iodine solution to be titrated and dilute to 300 mL with water. Titrate with 0.025N standardized phenylarsine oxide or 0.025N sodium thiosulfate until the amber color fades to yellow. Add starch indicator solution. Continue titration drop by drop until the blue color disappears. Run in replicate. Calculate the normality as follows:

$$Iodine\ concentration\ (eq/L) = \frac{V \times N}{S}$$

V = volume of titrant (mL)
N = normality of titrant (eq/L)
S = volume of iodine solution (mL)

5.11 Sodium Sulfide Nonahydrate, $Na_2S \cdot 9H_2O$ -- For the preparation of standard solution to be used for calibration curves. Standards must be prepared at pH >9 or <11. Protect standard from exposure to oxygen by preparing it without headspace. If standards are for use with the SIE, prepare in 20 percent SAOB. These standards are unstable and must be standardized immediately before use by either an iodometric titration or potentiometric titration.

5.12 Tin(II) chloride, $SnCl_2$, granular.

5.13 Titrants.

5.13.1 Standard phenylarsine oxide (PAO) solution (0.025N), -- This solution is commercially available.

CAUTION: PAO is toxic.

5.13.2 Standard Sodium Thiosulfate Solution (0.025N) -- Dissolve 6.205 ± 0.005 g $Na_2S_2O_3 \cdot 5H_2O$ in 500 mL water. Add 9 mL 1N NaOH and dilute to 1 liter.

5.13.3 Standard Silver Nitrate Solution (0.10N) -- Dissolve 16.989 g of $AgNO_3$ (dried for 2 hours at 150°C) in water and dilute to 1 L. Store in a brown bottle. Standardize weekly against standard sodium chloride solution.

5.14 Sodium Hydroxide (6N), NaOH -- Dissolve 240 g of sodium hydroxide in 1 liter of water.

5.15 Sulfide Anti-Oxidant Buffer (SAOB) -- Dissolve 80 g NaOH, 320 g sodium salicylate and 72 g ascorbic acid in 1 L water. Prepare fresh weekly.

5.16 Standard Sodium Chloride Solution (0.100N) -- Dissolve 5.84 g NaCl (dried for 2 hours at 140°C) in water and dilute to 1 L.

5.17 Potassium Chromate Indicator Solution -- Dissolve 50 g K_2CrO_4 in a little water. Add $AgNO_3$ solution until a definite red precipitate is formed. Let stand 12 hours, filter, and dilute to 1 L.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of the EPA test methods for evaluating solid waste (SW-846).

6.2 All aqueous and effluents must be preserved with zinc acetate and sodium hydroxide. Use four drops of 2N zinc acetate solution per 100 mL of sample. Adjust the pH to greater than 9 with 6N sodium hydroxide solution. Fill the sample bottle completely and stopper with a minimum of aeration. The treated sample is relatively stable and can be held for up to 7 days. If high concentrations of sulfide are expected to be in the sample, continue adding zinc acetate until all the sulfide has precipitated. For solid samples, fill the surface of the solid with 2N zinc acetate until moistened. Samples must be cooled to 4°C and stored headspace free.

6.3 Sample Preparation

6.3.1 For an efficient distillation, the mixture in the distillation flask must be of such a consistency that the motion of the stirring bar is sufficient to keep the solids from settling. The mixture must be free of solid objects that could disrupt the stirring bar. Prepare the sample using one of the procedures in this section then proceed with the distillation step (Section 7.0).

6.3.2 If the sample is aqueous, shake the sample container to suspend any solids, then quickly decant the appropriate volume (up to 250 mL) of the sample to a graduated cylinder, weigh the cylinder, transfer to the distillation flask and reweigh the cylinder to the nearest milligram. Be sure that a representative aliquot is used, or use the entire sample.

6.3.3 If the sample is aqueous but contains soft clumps of solid, it may be possible to break the clumps and homogenize the sample by placing the sample container on a jar mill and tumble or roll the sample for a few hours. The slurry may then be aliquoted and weighed as above to the nearest milligram then diluted with water up to a total volume of 250 mL to produce a mixture that is completely suspended by the stirring bar.

6.3.4 If the sample is primarily aqueous, but contains a large proportion of solid, the sample may be roughly separated by phase and the amount of each phase measured and weighed to the nearest milligram into the distillation flask in proportion to their abundance in the sample. Water may be added up to a total volume of 250 mL. As a guideline, no more than 25 g dry weight or 50 g of sludge can be adequately suspended in the apparatus.

6.3.5 If the sample contains solid objects that can not be reduced in size by tumbling, the solids must be broken manually. Clay-like solids should be cut with a spatula

or scalpel in a crystallizing dish. If the solids can be reduced to a size that they can be suspended by the stirring bar, the solid and liquid can be proportionately weighed.

6.3.6 Non-porous harder objects, for example stones or pieces of metal, may be weighed and discarded. The percent weight of non-porous objects should be used in the calculation of sulfide concentration if it has a significant effect on the reported result.

7.0 PROCEDURE

For acid-soluble sulfide samples, go to 7.1.

For acid-insoluble sulfide samples, to 7.2.

7.1 Acid-Soluble Sulfide

7.1.1 In a preliminary experiment, determine the approximate amount of sulfuric acid required to adjust a measured amount of the sample to pH less than or equal to 1. The sample size should be chosen so that it contains between 0.2 and 50 mg of sulfide. Place a known amount of sample or sample slurry in a beaker. Add water until the total volume is 200 mL. Stir the mixture and determine the pH. Slowly add sulfuric acid until the pH is less than or equal to 1.

CAUTION: Toxic hydrogen sulfide may be generated from the acidified sample. This operation must be performed in the hood and the sample left in the hood until the sample has been made alkaline or the sulfide has been destroyed. From the amount of sulfuric acid required to acidify the sample and the mass or volume of the sample acidified, calculate the amount of acid required to acidify the sample to be placed in the distillation flask.

7.1.2 Prepare the gas evolution apparatus as shown in Figure 1 in a fume hood.

7.1.3 Prepare a hot water bath at 70°C by filling a crystallizing dish or other suitable container with water and place it on a hot plate stirrer. Place a thermometer in the bath and monitor the temperature to maintain the bath at 70°C.

7.1.4 Assemble the three neck 500 mL flask, fritted gas inlet tube, and exhaust tube. Use Teflon sleeves to seal the ground glass joints. Place a Teflon coated stirring bar into the flask.

7.1.5 If determining sulfide by titration, place into each gas scrubbing bottle 10 ± 0.5 mL of the 0.5M zinc acetate solution, 5.0 ± 0.1 mL of 37 percent formaldehyde and 100 ± 5.0 mL water.

7.1.6 If determining sulfide by SIE, place into each gas scrubbing bottle 10.0 mL SAOB solution and 40.0 mL water.

7.1.7 Connect the gas evolution flask and gas scrubbing bottles as shown in Figure 1. Secure all fittings and joints.

7.1.8 Carefully place an accurately-weighed sample which contains 0.2 to 50 mg of sulfide into the flask. If necessary, dilute to approximately 200 mL with water.

7.1.9 Place the dropping funnel onto the flask making sure its stopcock is closed. Add the volume of sulfuric acid calculated in Step 7.7.1 plus an additional 50 mL into the dropping funnel. The bottom stopcock must be closed.

7.1.10 Attach the nitrogen inlet to the top of the dropping funnel gas shut-off valve. Turn on the nitrogen purge gas and adjust the flow through the sample flask to 25 mL/min. The nitrogen in the gas scrubbing bottles should bubble at about five bubbles per second. Nitrogen pressure should be limited to approximately 10 psi to prevent excess stress on the glass system and fittings. Verify that there are not leak in the system. Open the nitrogen shut-off valve leading to the dropping funnel. Observe that the gas flow into the sample vessel will stop for a short period while the pressure throughout the system equalizes. If the gas flow through the sample flask does not return within a minute, check for leaks around the dropping funnel. Once flow has stabilized, turn on magnetic stirrer. Purge system for 15 minutes with nitrogen to remove oxygen.

7.1.11 Heat sample to 70°C. Open dropping funnel to a position that will allow a flow of sulfuric acid of approximately 5 mL/min. Monitor the system until most of the sulfuric acid within the dropping funnel has entered the sample flask. Solids which absorb water and swell will restrict fluid motion and, therefore, lower recovery will be obtained. Such samples should be limited to 25 g dry weight.

7.1.12 Purge, stir, and maintain a temperature of 70°C for a total of 90 minutes from start to finish. Shut off nitrogen supply. Turn off heat.

7.1.13 Proceed to Step 7.3 for the analysis of the zinc sulfide by titration and to Step 7.4 for the analysis of sulfide by SIE.

7.2 Acid-Insoluble Sulfide

7.2.1 As the concentration of HCl during distillation must be within a narrow range for successful distillation of H_2S, the water content must be controlled. It is imperative that the final concentration of HCl in the distillation flask be about 6.5N and that the sample is mostly suspended in the fluid by the action of the stirring bar. This is achieved by adding 50 mL of water, including water in the sample, 100 mL of 9.8N HCl, and the sample to the distillation flask. Solids which absorb water and swell will restrict fluid motion and, therefore, lower recovery will be obtained. Such sample should be limited to 25 g dry weight.

7.2.2 If the matrix is a dry solid, weigh a portion of the sample such that it contains 0.2 to 50 mg of sulfide. The solid should be crushed to reduce particle size to 1 mm or less. Add 50 mL of water.

7.2.3 If the matrix is aqueous, then a maximum of 50 g of the sample may be used. No additional water may be added. As none of the target compounds are volatile, drying the sample may be preferable to enhance the sensitivity by concentrating the sample. If less than 50 g of the sample is required to achieve the 0.2 to 50 mg of sulfide range for the test, then add water to a total volume of 50 mL.

7.2.4 If the matrix is a moist solid, the water content of the sample must be determined (Karl Fischer titration, loss on drying, or other suitable means) and the water in the sample included in the total 50 mL of water needed for the correct HCl concentration. For example, if a 20 g sample weight is needed to achieve the desired sulfide level of 0.2 to 50 mg and the sample is 50 percent water then 40 mL rather than 50 mL of water is added along with the sample and 100 mL of 9.8N HCl to the distillation flask.

7.2.5 Weigh the sample and 5 g $SnCl_2$ into the distillation flask. Use up to 50 mL of water, was calculated above, to rinse any glassware.

7.2.6 Assemble the distillation apparatus as in Figure 1. If the sulfide is determined by titration, place 100 ± 2.0 mL of zinc acetate/sodium acetate buffer solution and 5.0 ± 0.1 mL of 37 percent formaldehyde in each gas scrubbing bottle. Tighten the pinch clamps on the distillation flask joints.

7.2.7 If determining sulfide by SIE, place into each gas scrubbing bottle 10.0 mL SAOB solution and 40.0 mL water.

7.2.8 Make sure the stopcock is closed and then add 100 ± 1.0 mL of 9.8N HCl to the dropping funnel. Connect the nitrogen line to the top of the funnel and turn the nitrogen on to pressurize the dropping funnel headspace.

7.2.9 Set the nitrogen flow at 25 mL/min. The nitrogen in the gas scrubbing bottles should bubble at about five bubbles per second. Purge the oxygen from the system for about 15 minutes.

7.2.10 Turn on the magnetic stirrer. Set the stirring bar to spin as fast as possible. The fluid should form a vortex. If not, the distillation will exhibit poor recovery. Add all of the HCl from the dropping funnel to the flask.

7.2.11 Heat the water bath to the boiling point (100°C). The sample may or may not be boiling. Allow the purged distillation to proceed for 90 minutes at 100°C. Shut off nitrogen supply. Turn off heat.

7.3 Titration of Distillate

7.3.1 Pipet a known amount of standardized 0.025N iodine solution (See Step 5.10.3) in a 500 mL flask, adding an amount in excess of that needed to oxidize the sulfide. Add enough water to bring the volume to 100 mL. The volume of standardized iodine solution should be about 65 mL for samples with 50 mg of sulfide.

7.3.2 If the distillation for acid-soluble sulfide is being used, add 2 mL of 6N HCl. If the distillation for acid-insoluble sulfides is performed, 10 mL of 6 N HCl should be added to the iodine.

7.3.3 Pipet both of the gas scrubbing bottle solutions to the flask, keeping the end of the pipet below the surface of the iodine solution. If at any point in transferring the zinc acetate solution or rinsing the bottles, the amber color of the iodine disappears or fades to yellow, more 0.025N iodine must be added. This additional amount must be added to the amount from Step 7.3.1 for calculations. Record the total volume of standardized 0.025N iodine solution used.

7.3.4 Prepare a rinse solution of a known amount of standardized 0.025N iodine solution, 1 mL of 6N HCl, and water to rinse the remaining white precipitate (zinc sulfide) from the gas scrubbing bottles into the flask. There should be no visible traces of precipitate after rinsing.

7.3.5 Rinse any remaining traces of iodine from the gas scrubbing bottles with water, and transfer the rinses to the flask.

7.3.6 Titrate the solution in the flask with standard 0.025N phenylarsine oxide or 0.025N sodium thiosulfate solution until the amber color fades to yellow. Add enough starch indicator for the solution to turn dark blue and titrate until the blue color disappears. Record the volume of titrant added. Calculate the sulfide concentration as follows;

$$Sulfide\ (mg/L) = \frac{(V1 \times N1) - (V2 \times N2)}{S} \times K$$

V1 = volume of iodine solution (mL)
N1 = normality of iodine solution (eq/L)
V2 = volume of titrant added (mL)
N2 = normality of titrant (mL)
S = sample weight (kg)
K = 16.03 mg sulfide/meq sulfide

7.4 Sulfide SIE Measurement of Distillate

7.4.1 Standardization of Silver Nitrate -- Add 10.00 mL of 0.100N NaCl and 40 mL water to a 125 mL flask. Adjust pH to 7-10 with 6N NaOH solution. Add 1.0 mL potassium chromate indicator. Titrate with silver nitrate solution to a pinkish yellow end point. Be consistent with end point recognition. Repeat with a reagent blank (water and indicator). Calculate the normality of the silver nitrate as follows:

$$Silver\ nitrate\ conc.\ (eq/L) = \frac{(V1 - Vb) \times N}{V2}$$

V1 = volume of silver nitrate added for NaCl sample (mL)
Vb = volume of silver nitrate added for blank sample (mL)
N = normality of NaCl (eq/L)
V2 = volume of NaCl (10.00 mL)

7.4.2 Standardization of Sulfide Standards -- From the sodium sulfide salt, prepare standards with nominal concentrations of 10, 100, and 1,000 mg/L sulfide in a matrix of 20 percent SAOB. Standardize each solution immediately prior to calibrating the SIE. The standards may be calibrated by iodometric titration (described in section 7.3) or by potentiometric titration as described below.

The titration is monitored with a combination silver electrode (silver-coated platinum ring sensing electrode with a silver/silver chloride reference electrode).

Prior to use the electrode is conditioned by soaking in 2 percent sodium sulfide for 5 minutes, soaking in 10 percent sodium sulfide until the brownish layer becomes black, rinsing with water, and cleaning with a soft cloth. After conditioning, the electrode is connected to the pH/mV meter. 20 mL of a sulfide standard (or suitable quantity to get accurate titration) and 1 mL concentrated ammonia are pipetted into a titration vessel. The electrode is inserted and the potential recorded. The sample is titrated with the standardized silver nitrate until a potential of 100 mV is attained. The potential is recorded after each titrant addition. The equivalence point is determined from the first derivative of the titration curve. The sulfide concentration is then calculated as follows:

$$Sulfide\ conc.\ (mg/L) = \frac{A \times B \times K}{C}$$

A = volume of silver nitrate (mL)
B = normality of silver nitrate (eq/L)
K = 16,000 mg/meq
C = volume of sulfide standard (mL)

7.4.3 Calibration of Sulfide SIE and Meter -- Following the meter operating instructions, calibrate the meter directly in terms of concentration using the 10, 100, and 1,000 mg/L sulfide standards. The standards must be freshly standardized.

7.4.3.1 For meters which cannot be calibrated in terms of concentration, measure the mV reading for each of the standards. Prepare a calibration curve by plotting the mV vs. concentration on semi-log paper.

7.4.3.2 The measurement of the standards is performed by pouring 25 mL standard into a 50 mL beaker, adding a stir bar and gently stirring, and placing the sulfide SIE and reference electrode into the solution. The reading is recorded when stable.

7.4.4 Measurement of Sulfide in Unknown Samples -- Sulfide in unknown samples is determined with the SIE as follows:

Rinse the electrodes with water, blot dry, pour 25 mL sample from the scrubber bottle into a 50 mL beaker, add a stir bar and stir gently, insert the electrodes, record the sulfide concentration (or mV reading) when a stable reading is obtained. If mV is recorded, calculate the sulfide concentration from the calibration curve.

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of 3 years. This method is restricted to use by or under supervision of experienced analysts. Refer to the appropriate section of Chapter One for additional quality control requirements.

8.2 A reagent blank should be run once in 20 analyses or per analytical batch, whichever is more frequent.

8.3 Check standards are prepared from water and a known amount of sodium sulfide. A check standard should be run with each analytical batch of samples, or once in 20 samples. Acceptable recovery will depend on the level.

8.4 A matrix spike sample should be run for each analytical batch or every 20 samples, whichever is more frequent, to determine matrix effects. If recovery is low, acid-insoluble sulfides are indicated. A matrix spike sample is a sample brought through the whole sample preparation and analytical process.

8.5 A laboratory control sample (LCS) must be analyzed with each batch of samples. An LCS is a sulfide standard which is processed exactly like a sample, including distillation. An LCS may be prepared in a sodium hydroxide matrix and precipitated with zinc acetate prior to distillation. The SAOB matrix may precipitate upon acidification and cause problems with the distillation. The acceptance criterion for percent recovery is 80-120 percent.

9.0 METHOD PERFORMANCE

9.1 Accuracy -- Accuracy for this method was determined by three independent laboratories by measuring percent recoveries of spikes for both clean matrices (water) and actual waste samples. The results are summarized below.

9.1.1 For Acid-Soluble Sulfide (Spiking levels ranged from 0.4 to 8 mg/L)

Accuracy of Titration Step Only -- Lab A 84-100 percent recovery, Lab B 110-122 percent recovery.

Accuracy of Sulfide SIE Step Only -- Lab D 75-105 percent recovery.

Accuracy for Entire Method for Clean Matrices (water) -- Lab 94-106 percent recovery.

Accuracy of Entire Method for Actual Waste Samples -- Lab C 77-92 percent recovery.

9.1.2 For Acid-Insoluble Sulfide (Spiking levels ranged from 2.2 to 22 mg/kg)

The percent recovery was not as thoroughly studied for acid-insoluble sulfide as it was for acid-soluble sulfide.

Accuracy of Entire Method for Synthetic Waste Samples -- Lab C 21-81 percent recovery.

9.2 Precision

9.2.1 For Acid-Soluble Sulfide

Precision of Titration Step Only -- Lab A Coefficient of Variation (CV) percent 2.0 to 37, Lab B CV percent 1.1 to 3.8.

Precision of Sulfide SIE Step Only -- Lab D CV percent 2.0 to 10.

Precision of Entire Method for Clean Matrices (water) -- Lab C CV percent 3.0 to 12.

Precision of Entire Method for Actual Waste Samples -- Lab C CV percent 0.86 to 45.

9.2.1 For Acid-Insoluble Sulfide

Precision of Entire Method with Synthetic Wastes -- Lab C CV percent 1.2 to 42.

9.3 Detection Limit

9.3.1 For the titration procedure, the detection limit was determined by analyzing seven replicates at 0.45 and 4.5 mg/L. The detection limit was calculated from the standard deviation times the student's t-value for one-tailed test with n-1 degrees of freedom at 99 percent confidence level. The detection limit for a clean matrix (water) was found to be between 0.2 and 0.4 mg/L.

9.3.2 For the sulfide SIE, the practical detection limit is about 1 mg/L. It is possible to detect lower quantities, however the electrode has a sluggish response below 1 mg/L.

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Gas Evolution Apparatus

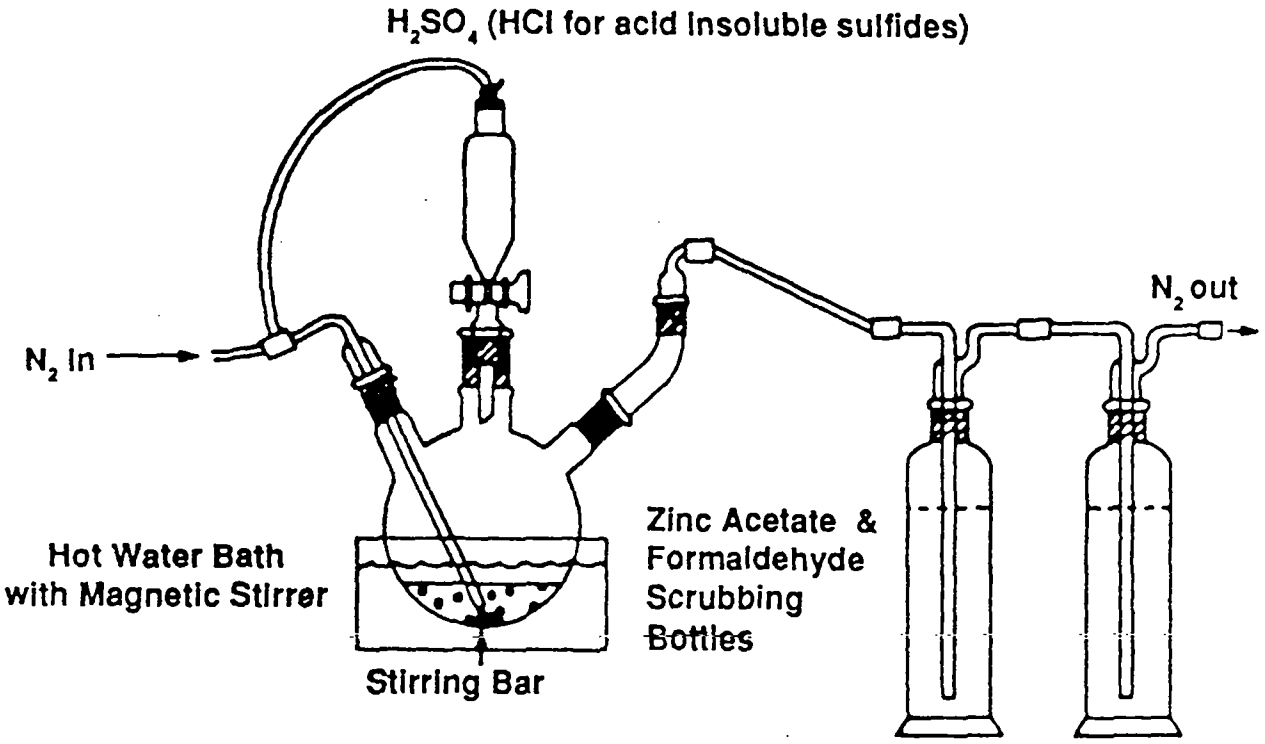
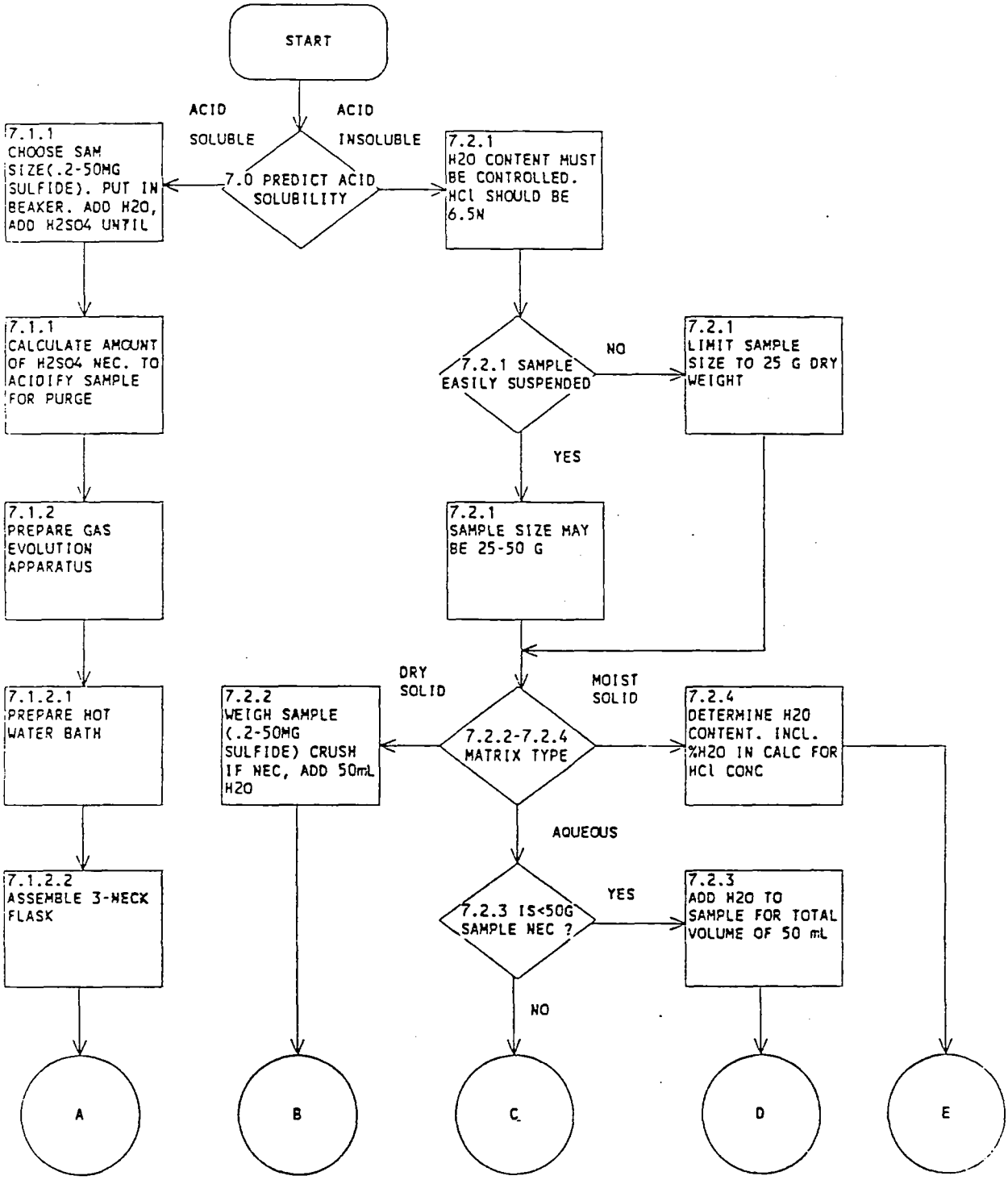
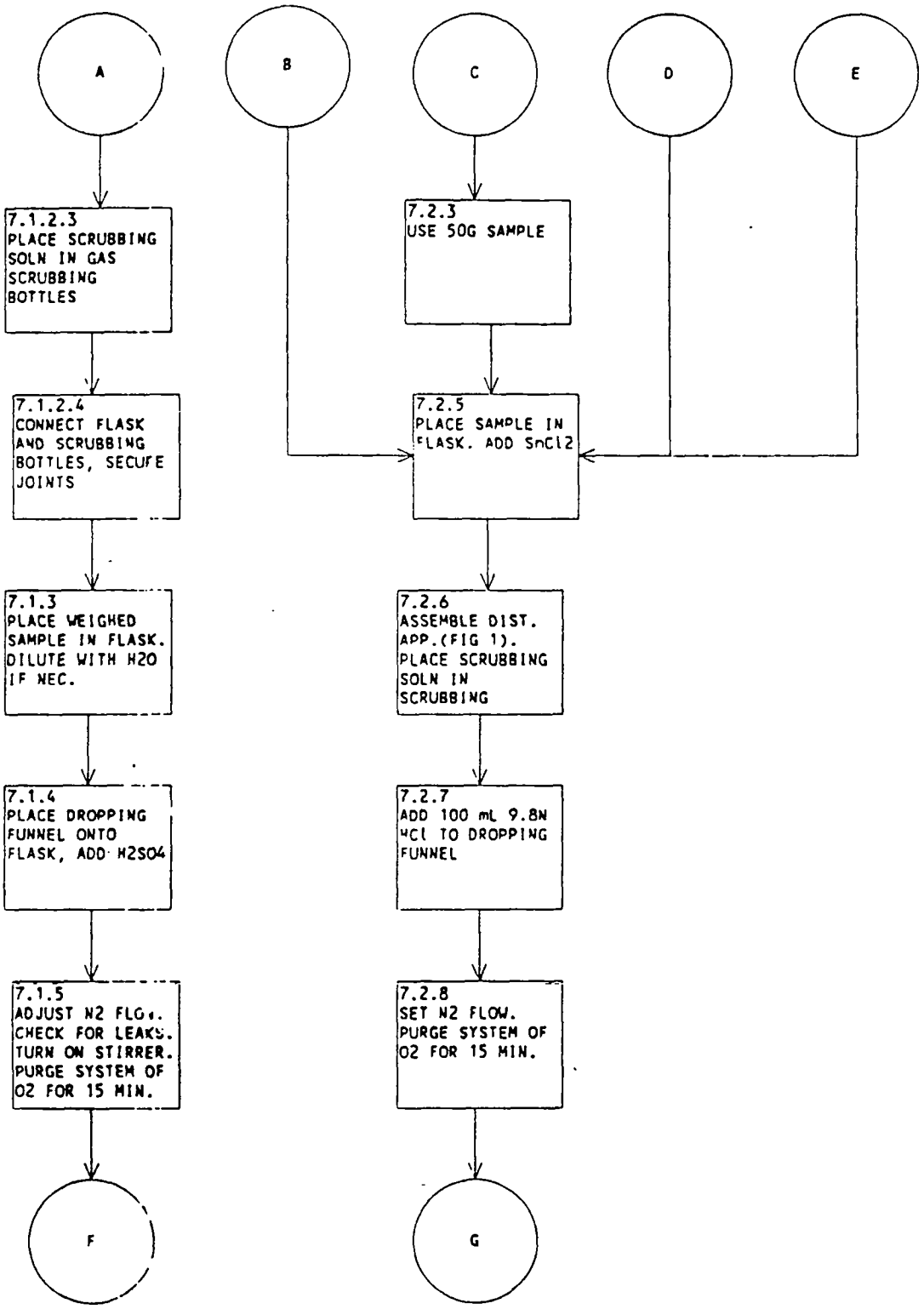
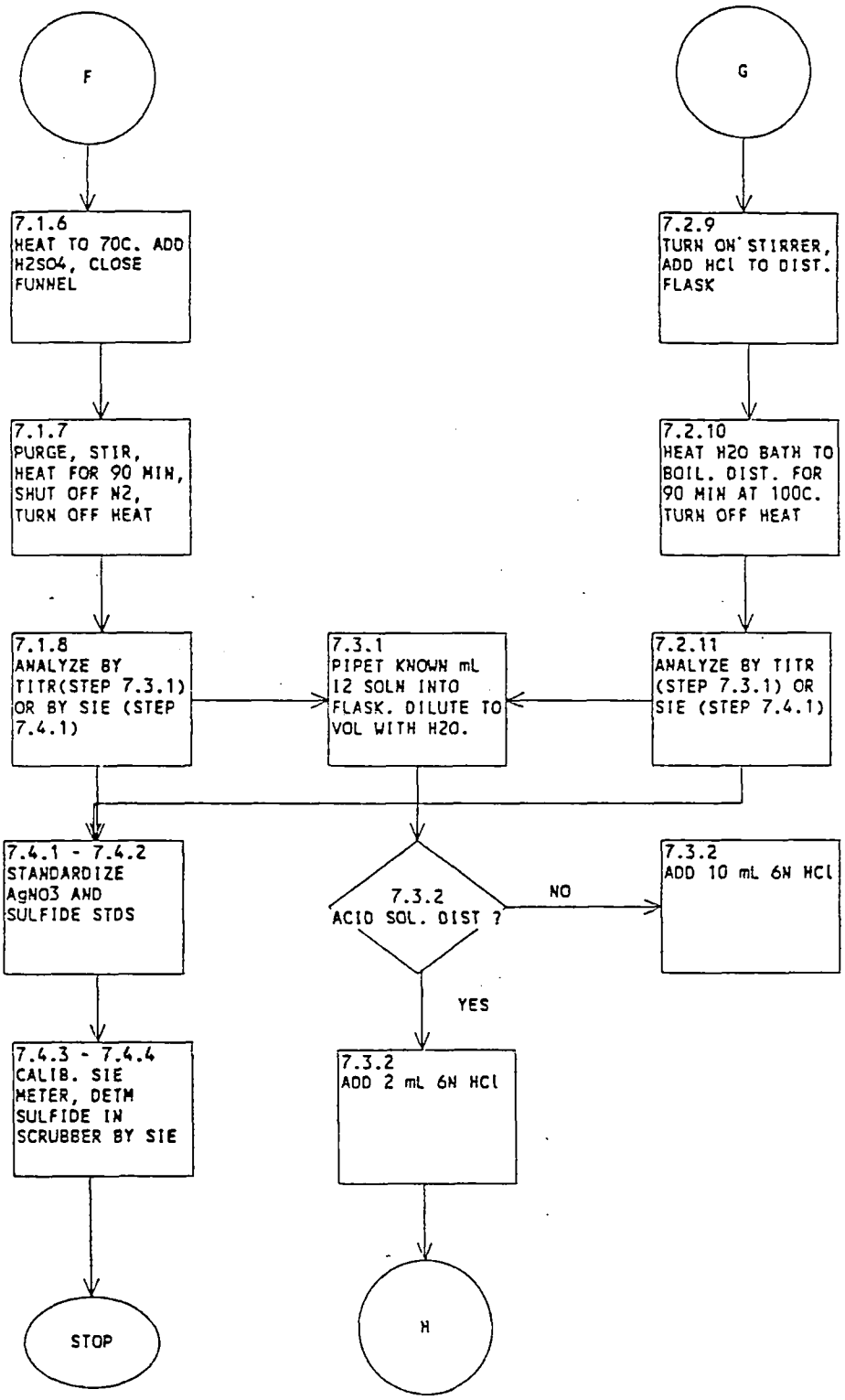
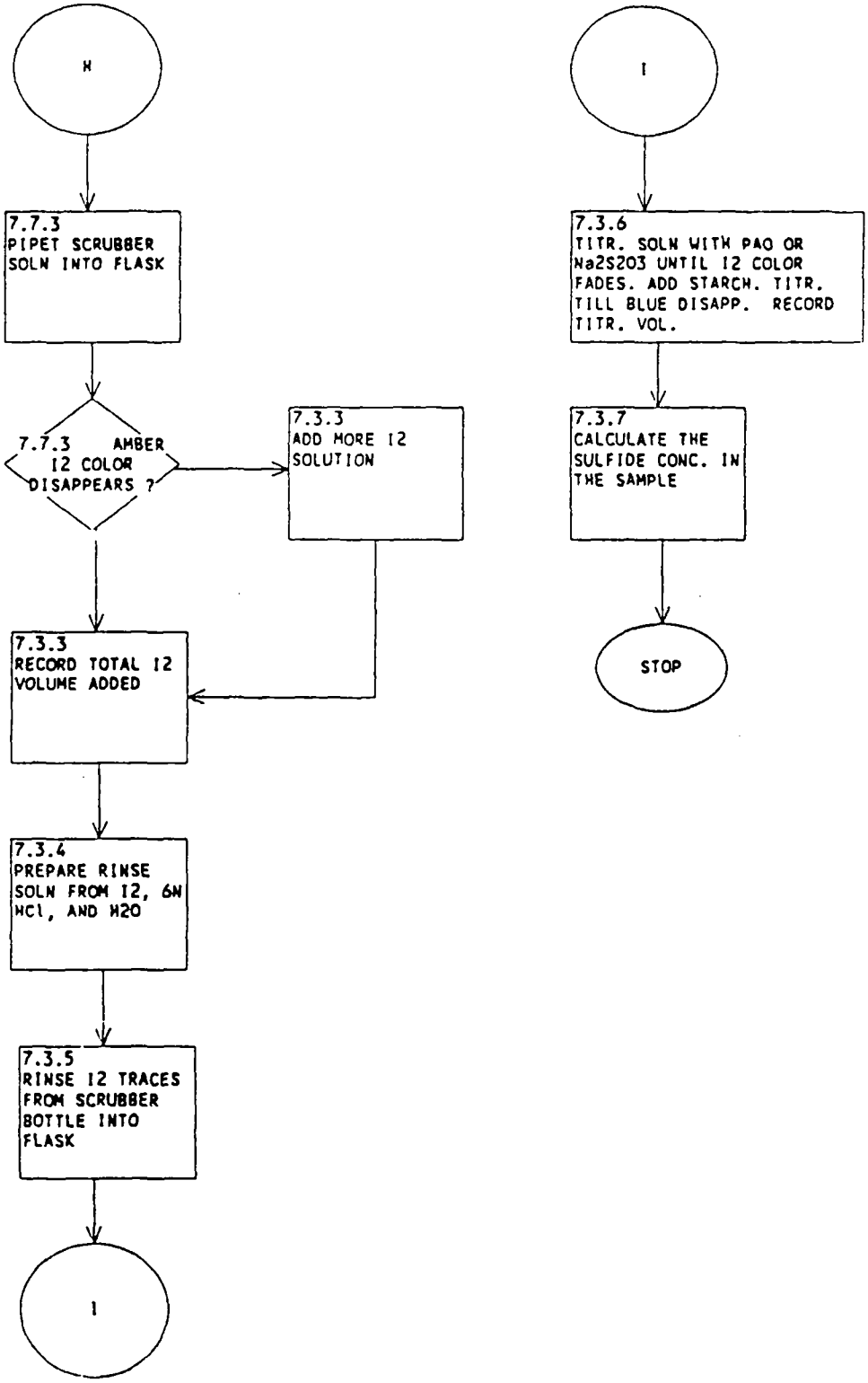


Figure 1.


START
ACID SOLUBLE
ACID INSOLUBLE
7.0 PREDICT ACID SOLUBILITY
7.1.1 CHOOSE SAM SIZE(.2-50MG SULFIDE). PUT IN BEAKER. ADD H2O, ADD H2SO4 UNTIL
7.2.1 H2O CONTENT MUST BE CONTROLLED. HCl SHOULD BE 6.5N
7.1.1 CALCULATE AMOUNT OF H2SO4 NEC. TO ACIDIFY SAMPLE FOR PURGE
7.2.1 SAMPLE EASILY SUSPENDED
NO
7.2.1 LIMIT SAMPLE SIZE TO 25 G DRY WEIGHT
YES
7.1.2 PREPARE GAS EVOLUTION APPARATUS
7.2.1 SAMPLE SIZE MAY BE 25-50 G
DRY SOLID
MOIST SOLID
7.1.2.1 PREPARE HOT WATER BATH
7.2.2 WEIGH SAMPLE (.2-50MG SULFIDE) CRUSH IF NEC, ADD 50mL H2O
7.2.2-7.2.4 MATRIX TYPE
7.2.4 DETERMINE H2O CONTENT. INCL. %H2O IN CALC FOR HCl CONC
AQUEOUS
7.1.2.2 ASSEMBLE 3-NECK FLASK
7.2.3 IS<50G SAMPLE NEC ?
YES
7.2.3 ADD H2O TO SAMPLE FOR TOTAL VOLUME OF 50 mL
NO
A
B
C
D
E


A
B
C
D
E
7.1.2.3
PLACE SCRUBBING SOLN IN GAS SCRUBBING BOTTLES
7.1.2.4
CONNECT FLASK AND SCRUBBING BOTTLES, SECURE JOINTS
7.1.3
PLACE WEIGHED SAMPLE IN FLASK. DILUTE WITH H2O IF NEC.
7.1.4
PLACE DROPPING FUNNEL ONTO FLASK, ADD H2SO4
7.1.5
ADJUST N2 FLOW. CHECK FOR LEAKS. TURN ON STIRRER. PURGE SYSTEM OF O2 FOR 15 MIN.
F
7.2.3
USE 50G SAMPLE
7.2.5
PLACE SAMPLE IN FLASK. ADD SnCl2
7.2.6
ASSEMBLE DIST. APP.(FIG 1). PLACE SCRUBBING SOLN IN SCRUBBING
7.2.7
ADD 100 mL 9.8N HCl TO DROPPING FUNNEL
7.2.8
SET N2 FLOW. PURGE SYSTEM OF O2 FOR 15 MIN.
G


F
G
7.1.6
HEAT TO 70C. ADD H2SO4, CLOSE FUNNEL
7.2.9
TURN ON STIRRER, ADD HCl TO DIST. FLASK
7.1.7
PURGE, STIR, HEAT FOR 90 MIN, SHUT OFF N2, TURN OFF HEAT
7.2.10
HEAT H2O BATH TO BOIL. DIST. FOR 90 MIN AT 100C. TURN OFF HEAT
7.1.8
ANALYZE BY TITR(STEP 7.3.1) OR BY SIE (STEP 7.4.1)
7.3.1
PIPET KNOWN mL I2 SOLN INTO FLASK. DILUTE TO VOL WITH H2O.
7.2.11
ANALYZE BY TITR (STEP 7.3.1) OR SIE (STEP 7.4.1)
7.4.1 - 7.4.2
STANDARDIZE AgNO3 AND SULFIDE STDS
7.3.2
ACID SOL. DIST ?
NO
7.3.2
ADD 10 mL 6N HCl
YES
7.4.3 - 7.4.4
CALIB. SIE METER, DETM SULFIDE IN SCRUBBER BY SIE
7.3.2
ADD 2 mL 6N HCl
STOP
H


H
7.7.3
PIPET SCRUBBER SOLN INTO FLASK
7.7.3 AMBER I2 COLOR DISAPPEARS ?
7.3.3
ADD MORE I2 SOLUTION
7.3.3
RECORD TOTAL I2 VOLUME ADDED
7.3.4
PREPARE RINSE SOLN FROM I2, 6N HCl, AND H2O
7.3.5
RINSE I2 TRACES FROM SCRUBBER BOTTLE INTO FLASK
I
I
7.3.6
TITR. SOLN WITH PAO OR Na2S2O3 UNTIL I2 COLOR FADES. ADD STARCH. TITR. TILL BLUE DISAPP. RECORD TITR. VOL.
7.3.7
CALCULATE THE SULFIDE CONC. IN THE SAMPLE
STOP

APPENDIX B

MODIFIED METHOD 9031

EXTRACTABLE INSOLUBLE SULFIDES

1.0 SCOPE AND APPLICATION

1.1 The extraction procedure described in this method is designed for the extraction of sulfides from matrices that are not directly amenable to the distillation procedure Method 9030. This method is also not applicable for reactive sulfide. Refer to Chapter Seven, Step 7.3.4.1 for the determination of reactive sulfide. This method is applicable to oil, soil, multiphasic, and all other matrices not amenable to analysis by Method 9030.

1.2 Method 9031 is suitable for measuring sulfide in solid samples at concentrations above 1 mg/kg.

2.0 SUMMARY OF METHOD

2.1 If the sample contains solids that will interfere with agitation and homogenization of the sample mixture, or so much oil or grease as to interfere with the formation of a homogeneous emulsion in the distillation procedure, the sample must be filtered and the solids extracted with water at pH>9 or <11. The extract is then combined with the filtrate and analyzed by the distillation procedure. Separation of sulfide from the sample matrix is accomplished by the addition of sulfuric acid to the sample. The sample is heated to 70°C and the hydrogen sulfide (H_2S) which is formed is distilled under acidic conditions and carried by a nitrogen stream into gas scrubbing bottles. If the sulfide is to be determined by titration, the gas scrubbers contain zinc acetate where it is precipitated as zinc sulfide. If the sulfide is determined by sulfide ion specific electrode (SIE), the gas scrubbers contain sulfide anti-oxidant buffer (SAOB, a sodium hydroxide solution containing salicylic and ascorbic acids at a pH>12) where it is trapped as sulfide ion.

2.2 If determined by titration the sulfide in the zinc sulfide precipitate is oxidized to sulfur with a known amount of excess iodine. Then the excess iodine is determine by titration with a standard solution of phenylarsine oxide (PAO) or sodium thiosulfate until the blue iodine starch complex disappears. The use of standard sulfide solutions is not possible because of their instability to oxidative degradation. Therefore quantitation is based on the PAO or sodium thiosulfate.

If determined by sulfide SIE, the sulfide in the SAOB is determined directly with a calibrated sulfide SIE. The sulfide SIE is calibrated using freshly standardized sulfide standards in a SAOB matrix (to minimize degradation prior to calibration). The sulfide standards are standardized by either a thiosulfate or silver nitrate titration.

3.0 INTERFERENCES

3.1 Samples with aqueous samples must be taken with a minimum of aeration to avoid volatilization of sulfide or reaction with oxygen, which oxidizes sulfide to sulfur compounds that are not detected.

3.2 Sulfur compounds, such as sulfite and hydrosulfite, decompose in acid, and may form sulfur dioxide. This gas may be carried over to the zinc acetate gas scrubbing bottles and subsequently react with the iodine solution yielding false high value. The addition of formaldehyde into the zinc acetate gas scrubbing bottles removes this interference. Any sulfur dioxide entering the scrubber will form an addition compound with the formaldehyde which is unreactive towards the iodine in the acidified mixture. This methods shows no sensitivity to sulfite or hydrosulfite at concentrations up to 10 mg/kg of the interferant.

3.3 The iodometric method suffers interference from reducing substances that react with iodine, including thiosulfate, sulfite, and various organic compounds. The SIE method is free from interferences.

3.4 Interferences have been observed when analyzing samples with high metal content such as electroplating waste and chromium containing tannery waste, and interference.

4.0 APPARATUS AND MATERIALS

4.1 Extractor – Any suitable device that sufficiently agitates a sealed container of 1 liter volume or greater. For the purpose of this analysis, agitation is sufficient when all sample surfaces are continuously brought into contact with extraction fluid, and the agitation prevents stratification of the sample and fluid. Examples of suitable extractors are shown in Figures 2 and 3. The tumble-extractors turn the extraction bottles end-over-end at a rate of about 30 rpm. The apparatus in Figure 2 may be easily fabricated from plywood. The jar compartments must be padded with polyurethane foam to absorb shock. The drive apparatus is a Norton jar mill.

4.2 Buchner funnel apparatus

4.2.1 Buchner Funnel--500 mL capacity, with 1 liter vacuum filtration flask.

4.2.2 Glass Wool--Suitable for filtering, 0.8 um diameter such as Corning Pyrex 3950.

4.2.3 Vacuum Source--Preferably a water driven aspirator. A valve or stopcock to release vacuum is required.

4.3 Distillation apparatus as shown in Figure 1.

4.3.1 Three Neck Flask -- 500 mL, 24/40 standard tapered joints.

4.3.2 Dropping Funnel -- 100 mL, 24/40 outlet joint.

4.3.3 Purge Gas Inlet Tube -- 24/40 joint, with coarse frit.

4.3.4 Purge Gas Inlet Tube -- 24/40 joint, with coarse frit.

4.3.5 Gas Scrubbing Bottles -- 125 mL, with ¼ in. o.d. inlet and outlet tubes. Impinger tub must be fritted.

4.3.6 Tubing -- ¼ in. o.d. Teflon or polypropylene. Do not use rubber.

4.4 Hot plate stirrer

4.5 pH/mV/ion meter capable of reading to 0.1 mV

4.6 Nitrogen regulator

4.7 Flowmeter

4.8 Separatory Funnels -- 500 mL.

4.9 Tumbler -- See Figures 2 and 3.

4.10 Sulfide SIE

4.11 Double-junction reference electrode (silver/silver chloride)

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 ASTM Type II Water (ASTM D-1193-77 (1983)) -- All waster used in this method will be Type II unless otherwise specified.

5.3 Zinc Acetate Solution for Sample Preservation (2N) -- Dissolve 220 g of zinc acetate dihydrate in 500 mL of water.

5.4 Sodium Hydroxide (50 percent w/v in water), NaOH -- Commercially available.

5.5 Tin (II) Chloride, $SnCl_2 \cdot 2H_2O$, granular.

5.6 n-Hexane

5.7 Nitrogen gas

5.8 Sulfuric Acid (concentrated), H_2SO_4.

5.9 Zinc Acetate for the Scrubber (approximately 0.5M)

Dissolve about 110 g zinc acetate dihydrate in 200 mL of water. Add 1 mL hydrochloric acid (concentrated), HCl, to prevent precipitation of zinc hydroxide. Dilute to 1 liter.

5.10 Formaldehyde (37 percent solution).

5.11 Starch Solution -- Use either an aqueous solution or a soluble starch powder mixture. Prepare an aqueous solution as follows; Dissolve 2 g soluble starch and 2 g salicylic acid (as a preservative) in 100 mL hot water.

5.12 Iodine Solution (approximately 0.025N) -- Dissolve 25 g potassium iodide, KI, in 700 mL of water in a 1 liter volumetric flask. Add 3.2 g iodine and allow to dissolve. Dilute to 1 liter and standardize as follows. Dissolve approximately 2 g KI in 150 mL of water. Pipet exactly 20 mL of the iodine solution to be titrated and dilute to 300 mL with water. Titrate with 0.025N standardized phenylarsine oxide or 0.025N sodium thiosulfate until the amber color fades to yellow. Add starch indicator solution. The solution will turn deep blue. Continue titration drop by drop until the blue color disappears. Run in replicate. Calculate the normality as follows:

$$Iodine\ conc.\ (eq/L) = \frac{Vt \times Nt}{Vi}$$

Vt = volume of titrant (mL)
Nt = normality of titrant (eq/L)
Vi = volume of iodine solution (20.00 mL)

5.13 Sodium Sulfide Nonahydrate, $Na_2S \cdot 9H_2O$ -- For the preparation of standard solution to be used for calibration curves. Standards must be prepared at pH >9 or <11. Protect standard from exposure to oxygen by preparing it without headspace. If standards are for use with the SIE, prepare in 20 percent SAOB. These standards are unstable and must be standardized immediately before use by either an iodometric titration or potentiometric titration.

5.14 Titrants.

5.14.1 Standard phenylarsine oxide solution (PAO) (0.025N) -- This solution is commercially available.

CAUTION: PAO is toxic.

5.14.2 Standard Sodium Thiosulfate Solution (0.025N) -- Dissolve 6.205 ± 0.005 g $Na_2S_2O_3 \cdot 5H_2O$ in 500 mL water. Add 9 mL 1N NaOH and dilute to 1 liter.

5.14.3 Standard Silver Nitrate Solution (0.10N). Dissolve 16.989 g of $AgNO_3$ (dried for 2 hours at 150°C) in water and dilute to 1,000 L. Store in a brown bottle. Standardize weekly against standard sodium chloride solution.

5.15 Sulfide Anti-Oxidant Buffer (SAOB) -- Dissolve 80 g NaOH, 320 g sodium salicylate and 72 g ascorbic acid in 1 L water. Prepare fresh weekly.

5.16 Standard Sodium Chloride Solution (0.100N) -- Dissolve 5.84 g NaCl (dried for 2 hours at 140°C) in water and dilute to 1,000 L.

5.17 Potassium Chromate Indicator Solution -- Dissolve 50 g K_2CrO_4 in a little water. Add $AgNO_3$ solution until a definite red precipitate is formed. Let stand 12 hours, filter, and dilute to 1 L.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of the EPA test methods for evaluating solid waste (SW-846).

6.2 All samples must be preserved with zinc acetate and sodium hydroxide. Use four drops of 2N zinc acetate solution per 100 mL of sample. Adjust the pH to greater than 9 with 50 percent NaOH. Fill the sample bottle completely and stopper with a minimum of aeration. For solid samples, fill the surface of the solid with 2N zinc acetate until moistened. Samples must be cooled to 4°C during storage.

7.0 PROCEDURE

7.1 Assemble the Buchner funnel apparatus. Unroll the glass wool and fold the fiber over itself several times to make a pad about 1 cm thick when lightly compressed. Cut the pad to fit the Buchner funnel. Dry and weigh the pad, then place it in the funnel. Turn on the aspirator and wet the pad with a known amount of water.

7.2 Transfer a sample that contains between 1 and 50 mg of sulfide to the Buchner funnel. Rinse the sample container with known amounts of water and add the rinses to the Buchner funnel. When no free water remains in the funnel, slowly open the stopcock to allow air to enter the vacuum flask. A small amount of sediment may have passed through the glass fiber pad. This will not interfere with the analysis.

7.3 Transfer the solid and the glass fiber pad to a dried tared weighing dish. Since most greases and oils will not pass through the fiber pad, solids, oils, and greases will be extracted together. If the filtrate includes an oil phase, transfer the filtrate to a separatory funnel. Collect and measure the volume of the aqueous phase. Transfer the oil phase to the weighing dish with the solid and glass fiber pad.

7.4 Weight the dish containing solid, oil (if any) and glass fiber pad. Subtract the weight of the dry glass fiber pad. Calculate the volume of water present in the original sample by subtracting the total volume of rinses from the measured volume of the filtrate.

7.5 Place the following in a 1 liter wide-mouth bottle:

500 mL water
5 mL 50 percent w/v NaOH
1 g $SnCl_2 \cdot 2H_2O$
50 mL n-hexane (if an oil or grease is present).

Cap the bottle with a Teflon- or polyethylene-lined cap and shake vigorously to saturate the solution with stannous chloride. Direct a stream of nitrogen gas at about 10 mL/min into the bottle for about 1 minute to purge the headspace of oxygen. If the weight of the solids (Step 7.4) is greater than 25 g, weigh out a representative aliquot of 25 g and add it to the bottle while still purging with nitrogen. Otherwise, add all of the solids. Cap the bottle; avoid the influx of air.

7.6 The pH of the extract must be maintained at >9 or <11 throughout the extraction step and subsequent filtration. Since some samples may release acid, the pH must be monitored as follows. Shake the extraction bottle and wait 1 minute. Open the bottle

under a stream of nitrogen and check the pH. If the pH is below 9, add 50 percent NaOH in 5-mL increments until it is at least 9. Recap the bottle, and repeat the procedure until the pH does not drop. The bottle must be thoroughly purged of oxygen before each recapping. Oxygen will oxidize sulfide to elemental sulfur or other sulfur containing compounds that will not be detected.

7.7 Place the bottle in the tumbler, making sure there is enough foam insulation to cushion the bottle. Turn the tumbler on and allow the extraction to run for about 18 hours.

7.8 Prepare a Buchner funnel apparatus as in Step 7.1 with glass fiber pad filter.

7.9 Decant the extract to the Buchner funnel.

7.10 If the extract contains an oil phase, separate the aqueous phase using a separatory funnel. Neither the separation nor the filtration are critical, but are necessary to be able to measure the volume of the aqueous extract analyzed. Small amounts of suspended solids and oil emulsions will not interfere with the extraction.

7.11 At this point, an aliquot of the filtrate of the original sample may be combined with an aliquot of the extract in a proportion representative of the sample. Calculate the proportions as follows:

$$\frac{Af}{Ae} = \frac{Se}{St} \times \frac{Vs}{Vt}$$

Af = aliquot volume of the filtrate (mL)
Ae = aliquot volume of the extract (mL)
Se = mass (g) of solid extracted from step 7.5
St = total mass (g) of solid from step 7.4. Includes only weight of solids and oil.
Vs = total volume (mL) of sample filtrate from steps 7.1 and 7.2. Includes volume of all rinses.
Vt = total volume (mL) of extraction fluid from steps 7.5 and 7.6. Does not include hexane, which is later removed.

Alternatively, the samples may be analyzed separately, concentrations for each phase reported separately, and the amounts of each phase present in the sample reported separately.

7.12 Distillation of Sulfide

7.12.1 In a preliminary experiment, determine the approximate amount of sulfuric acid required to adjust a measured amount of the sample to pH less than or equal to 1. The sample size should be chosen so that it contains between 0.2 and 50 mg of sulfide. Place a known amount of sample or sample slurry in a beaker. Add water until the total volume is 200 mL. Stir the mixture and determine the pH. Slowly add sulfuric acid until the pH is less than or equal to 1.

CAUTION: Toxic hydrogen sulfide may be generated from the acidified sample. This operation must be performed in the hood and the sample left in the hood until the sample has been made alkaline or the sulfide has been destroyed.

From the amount of sulfuric acid required to acidify the sample and the mass or volume of the sample acidified, calculate the amount of acid required to acidify the sample to be placed in the distillation flask.

7.12.2 Prepare the gas evolution apparatus as shown in Figure 1 in a fume hood.

7.12.2.1 Prepare a hot water bath at 70°C by filling a crystallizing dish or other suitable container with water and place it on a hot plate stirrer. Place a thermometer in the bath and monitor the temperature to maintain the bath at 70°C.

7.12.2.2 Assemble the three neck 500 mL flask, fritted gas inlet tube, and exhaust tube. Use Teflon sleeves to seal the ground glass joints. Place a Teflon coated stirring bar into the flask.

7.12.2.3 If the sulfide is determined by titration, place into each gas scrubbing bottle 10 ± 0.5 mL of the 0.5M zinc acetate solution, 5.0 ± 0.1 mL of 37 percent formaldehyde and 100 ± 5.0 mL water.

If the sulfide is determined by SIE, place into each gas scrubbing bottle 10.0 mL SAOB solution and 40.0 mL water.

7.12.2.4 Connect the gas evolution flask and gas scrubbing bottles as shown in Figure 1. Secure all fittings and joints.

7.12.3 Carefully place an accurately weighed sample which contains 0.2 to 50 mg of sulfide into the flask. If necessary, dilute to approximately 200 mL with water.

7.12.4 Place the dropping funnel onto the flask making sure its stopcock is closed. Add the volume of sulfuric acid calculated in Step 7.7.1 plus an additional 50 mL into the dropping funnel. The bottom stopcock must be closed.

7.12.5 Attach the nitrogen inlet to the top of the dropping funnel gas shut-off valve. Turn on the nitrogen purge gas and adjust the flow through the sample flask to 25 mL/min. The nitrogen in the gas scrubbing bottles should bubble at about five bubbles per second. Nitrogen pressure should be limited to approximately 10 psi to prevent excess stress on the glass system and fittings. Verify that there are no leaks in the system. Open the nitrogen shut-off valve leading to the dropping funnel. Observe that the gas flow into the sample vessel will stop for a short period while the pressure throughout the system equalizes. If the gas flow through the sample flask does not return within a minute, check for leaks around the dropping funnel. Once flow has stabilized, turn on magnetic stirrer. Purge system for 15 minutes with nitrogen to remove oxygen.

7.12.6 Heat sample to 70°C. Open dropping funnel to a position that will allow a flow of sulfuric acid of approximately 5 mL/min. Monitor the system until most of the sulfuric acid within the dropping funnel has entered the sample flask. Close the dropping funnel while a small amount of acid remains. Immediately close the gas shut-off valve to the dropping funnel.

7.12.7 Purge, stir, and maintain a temperature of 70°C for a total of 90 minutes from start to finish. Shut off nitrogen supply. Turn off heat.

7.13 Titration of Distillate

7.13.1 Pipet a known amount of standardized 0.025N iodine solution (See Step 5.10.3) in a 500 mL flask, adding an amount in excess of that needed to oxidize the sulfide. Add enough water to bring the volume to 100 mL. The volume of standardized iodine solution should be about 65 mL for samples with 50 mg of sulfide.

7.13.2 Add 2 mL of 6N HCl.

7.13.3 Pipet both of the gas scrubbing bottle solutions to the flask, keeping the end of the pipet below the surface of the iodine solution. If at any point in transferring the zinc acetate solution or rinsing the bottles, the amber color of the iodine disappears or fades to yellow, more 0.025N iodine must be added. This additional amount must be added to the amount from Step 7.3.1 for calculations. Record the total volume of standardized 0.025N iodine solution used.

7.13.4 Prepare a rinse solution of a known amount of standardized 0.025N iodine solution, 1 mL of 6N HCl, and water to rinse the remaining white precipitate (zinc sulfide) from the gas scrubbing bottles into the flask. There should be no visible traces of precipitate after rinsing.

7.13.5 Rinse any remaining traces of iodine from the gas scrubbing bottles with water, and transfer the rinses to the flask.

7.13.6 Titrate the solution in the flask with standard 0.025N phenylarsine oxide or 0.025N sodium thiosulfate solution until the amber color fades to yellow. Add enough starch indicator for the solution to turn dark blue and titrate until the blue disappears. Record the volume of titrant used.

$$Sulfide\ conc.\ (mg/L) = \frac{(Vi \times Ni) - (Vt \times Nt)}{S} \times K$$

Vi = volume of iodine solution (mL)
Ni = normality of iodine solution (eq/L)
Vt = volume of titrant (mL)
Nt = normality of titrant (eq/L)
K = 16.03 mg sulfide/meq sulfide

7.14 Sulfide SIE Measurement of Distillate

7.14.1 Standardization of Silver Nitrate -- Add 10.00 mL of 0.100N NaCl and 40 mL water to a 125 mL flask. Adjust pH to 7-10 with dilute NaOH solution. Add 1.0 mL potassium chromate indicator. Titrate with silver nitrate solution to a pinkish yellow end point. Be consistent with end point recognition. Repeat with a reagent blank (water and indicator). Calculate the normality of the silver nitrate as follows;

$$Silver\ nitrate\ conc.\ (eq/L) = \frac{(V1 - Vb) \times N}{V2}$$

V1 = volume of silver nitrate added for NaCl sample (mL)
Vb = volume of silver nitrate added for blank sample (mL)
N = normality of NaCl (eq/L)
V2 = volume of NaCl (10.00 mL)

7.14.2 Standardization of Sulfide Standards -- From the sodium sulfide salt, prepare standards with nominal concentrations of 10, 100, and 1,000 mg/L sulfide in a matrix of 20 percent SAOB. Standardize each solution immediately prior to calibrating the SIE. The standards may be calibrated by iodometric titration (described in section 7.3) or by potentiometric titration as described below.

The titration is monitored with a combination silver electrode (silver-coated platinum ring sensing electrode with a silver/ silver chloride reference electrode). Prior to use the electrode is conditioned by soaking in 2 percent sodium sulfide for 5 minutes, soaking in 10 percent sodium sulfide until the brownish layer becomes black, rinsing with water, and cleaning with a soft cloth. After conditioning, the electrode is connected to the pH/mV meter. 20 mL of a sulfide standard (or suitable quantity to get accurate titration) and 1 mL concentrated ammonia are pipetted into a titration vessel. The electrode is inserted and the potential recorded. The sample is titrated with the standardized silver nitrate until a potential of 100 mV is attained. The potential is recorded after each titrant addition. The equivalence point is determined from the first derivative of the titration curve. The sulfide concentration is then calculated as follows:

$$Sulfide\ conc.\ (mg/L) = \frac{A \times B \times K}{C}$$

A = volume (mL) of silver nitrate
B = normality of silver nitrate (eq/L)
C = volume (mL) of sulfide standard
K = 16,000 mg/meq

7.14.3 Calibration of Sulfide SIE and Meter -- Following the meter operating instructions, calibrate the meter directly in terms of concentration using the 10, 100, and 1,000 mg/L sulfide standards. The standards must be freshly standardized.

For meters which cannot be calibrated in terms of concentration, measure the mV reading for each of the standards. Prepare a calibration curve by plotting the mV vs. concentration on semi-log paper.

The measurement of the standards is performed by pouring 25 mL standard into a 50 mL beaker, adding a stir bar and gently stirring, and placing the sulfide SIE and reference electrode into the solution. The reading is recorded when stable.

7.14.4 Measurement of Sulfide in Unknown Samples -- Sulfide in unknown samples is determined with the SIE as follows:

Rinse the electrodes with water, blot dry, pour 25 mL sample from the scrubber bottle into a 50 mL beaker, add a stir bar and stir gently, insert the electrodes,

record the sulfide concentration (or mV reading) when a stable reading is obtained. If mV is recorded, calculate the sulfide concentration from the calibration curve.

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of 3 years. This method is restricted to use by or under supervision of experienced analysts. Refer to the appropriate section of Chapter One for additional quality control requirements.

8.2 A reagent blank should be run once in 20 analyses or per analytical batch, whichever is more frequent.

8.3 Check standards are prepared from water and a known amount of sodium sulfide. A check standard should be run with each analytical batch of samples, or once in 20 samples. Acceptable recovery is 80-120 percent.

8.4 A matrix spike sample should be run for each analytical batch or every 20 samples, whichever is more frequent, to determine matrix effects. If recovery is low, acid-insoluble sulfides are indicated. A matrix spike sample is a sample brought through the whole sample preparation and analytical process.

8.5 Verify the calibration with an independently prepared QC reference sample every 20 samples or once per analytical batch, whichever is more frequent.

8.6 A laboratory control sample (LCS) must be analyzed with each batch of samples. An LCS is a sulfide standard which is processed exactly like a sample, including distillation. An LCS may be prepared in a sodium hydroxide matrix and precipitated with zinc acetate prior to distillation. The SAOB matrix may precipitate upon acidification and cause problems with the distillation. Acceptable recovery for the LCS is 80-120 percent.

9.0 METHOD PERFORMANCE

9.1 Accuracy -- Accuracy for this method was determine by three independent laboratories by measuring percent recoveries of spikes for both clean matrices (water) and actual waste samples. The results are summarized below.

Accuracy of entire method for four synthetic waste samples 70-104 percent recovery.

9.2 Precision -- Precision of entire method for four synthetic wastes. Percent coefficient of variation 1.0-3.4.

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Gas Evolution Apparatus

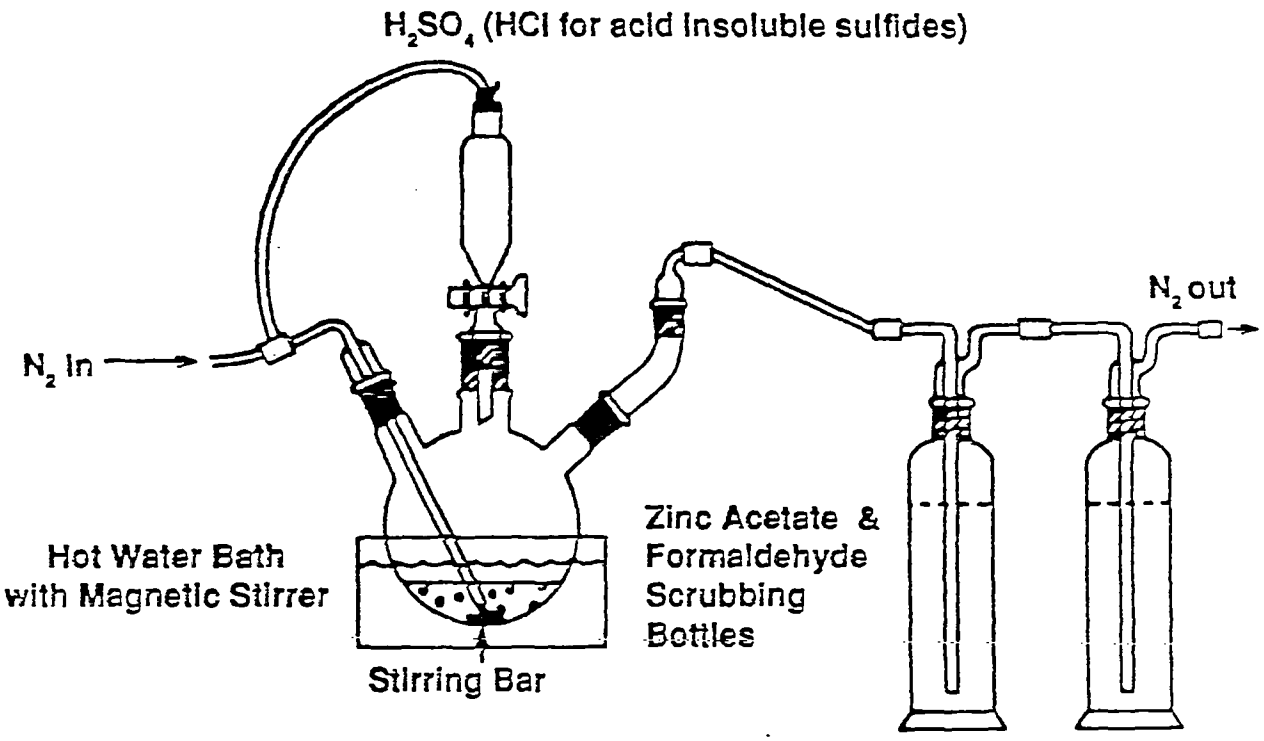


Figure 1.

Tumbler-Extractor

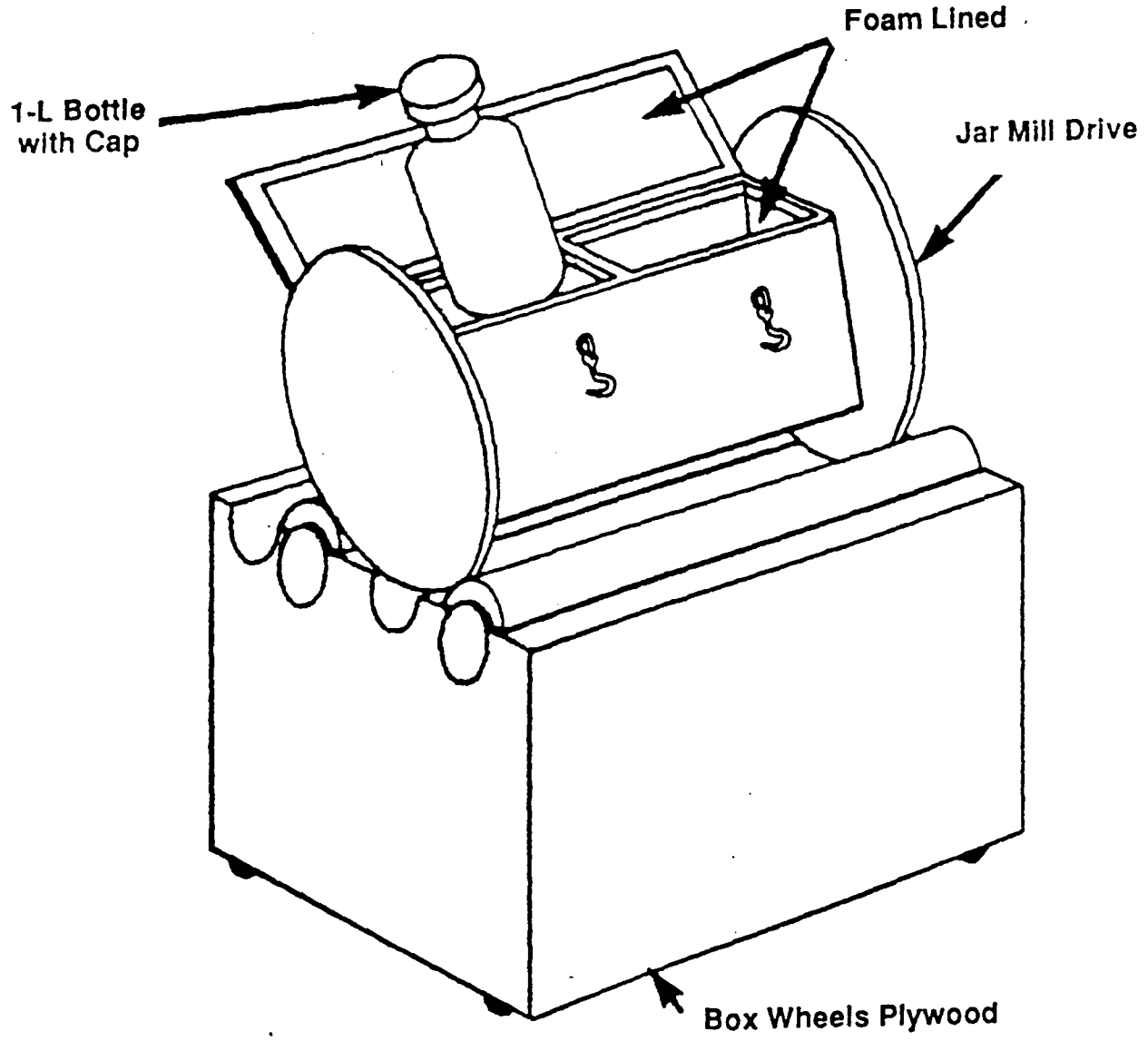


Figure 2.

Extractor

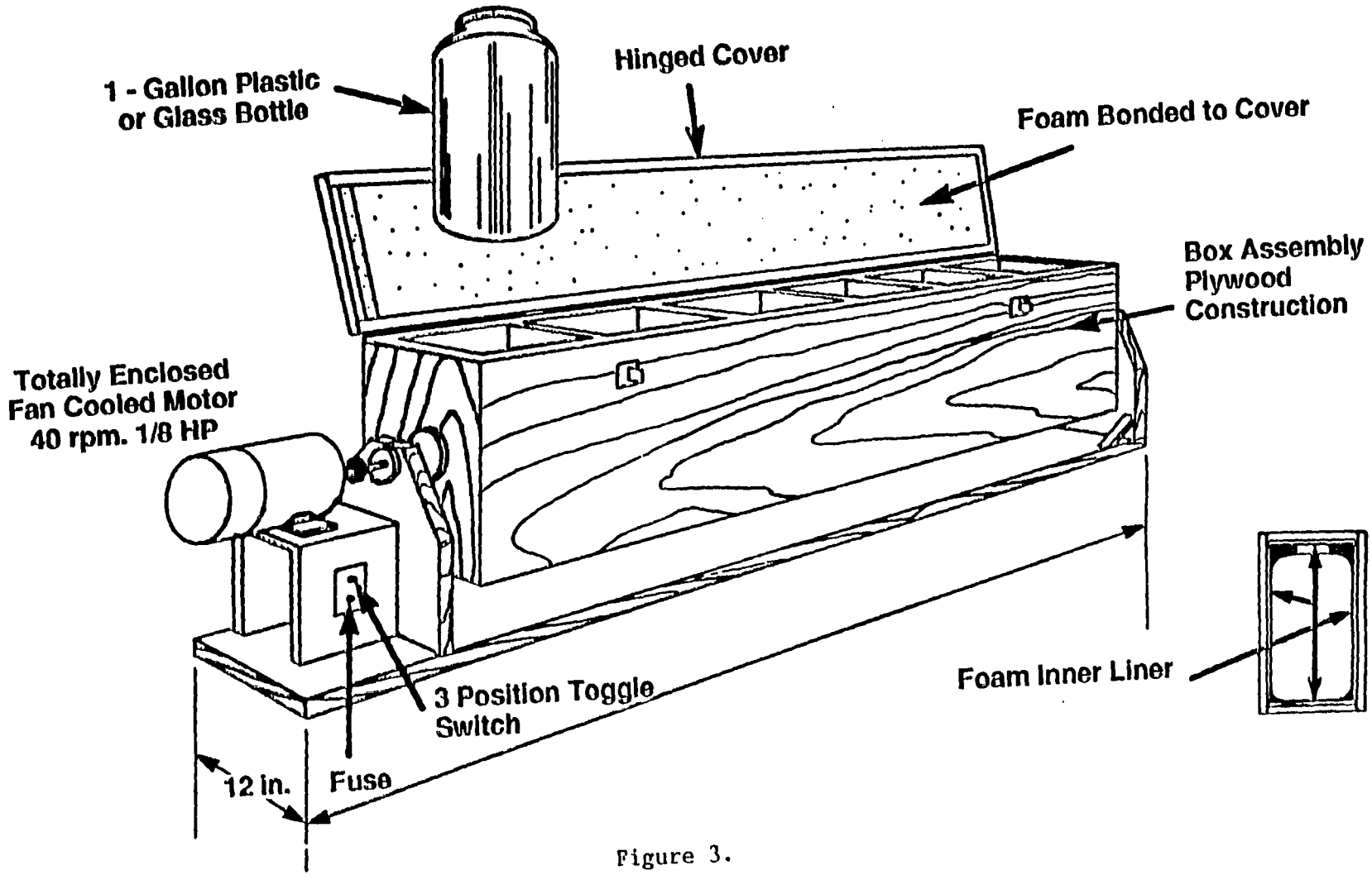
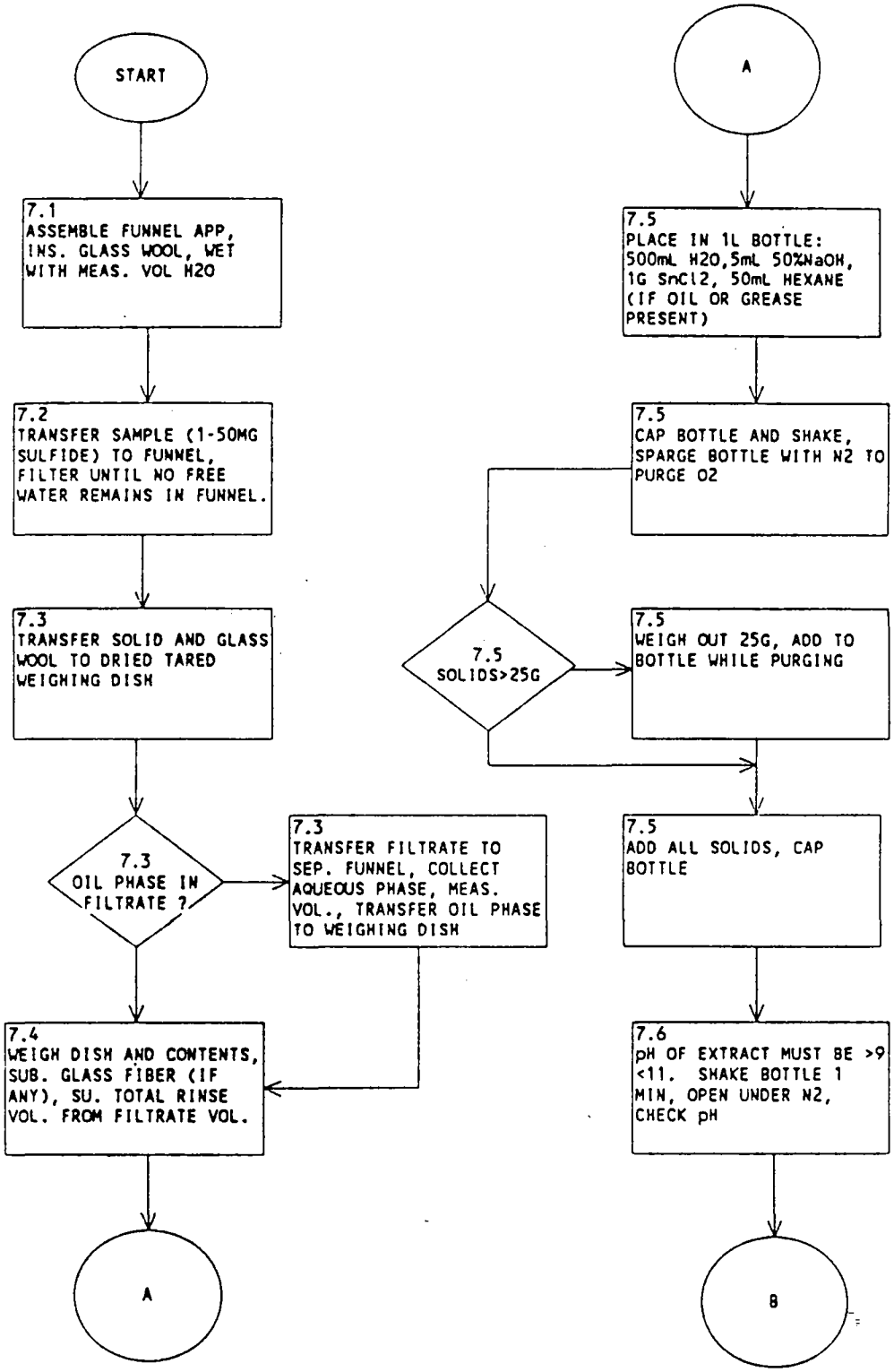
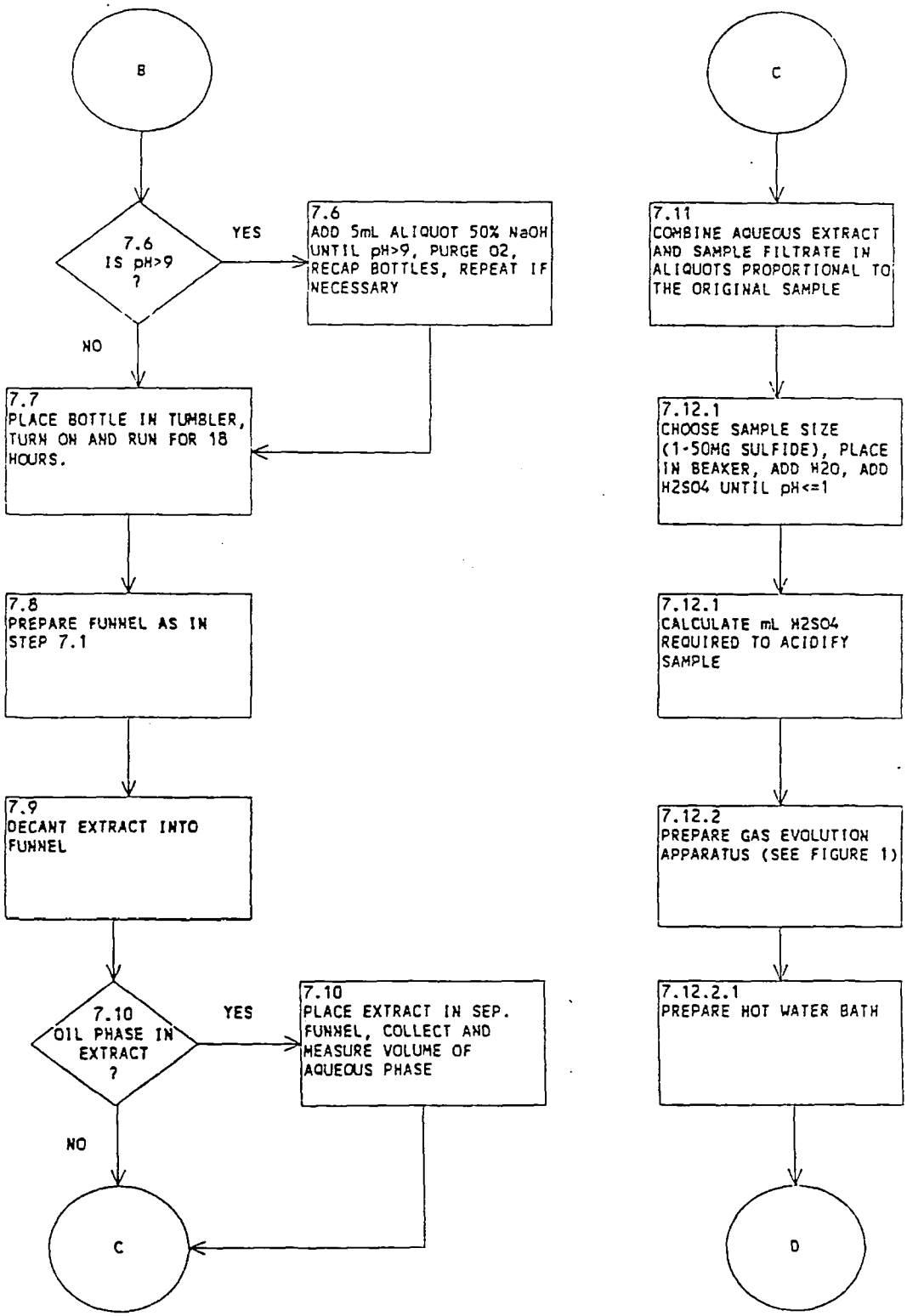
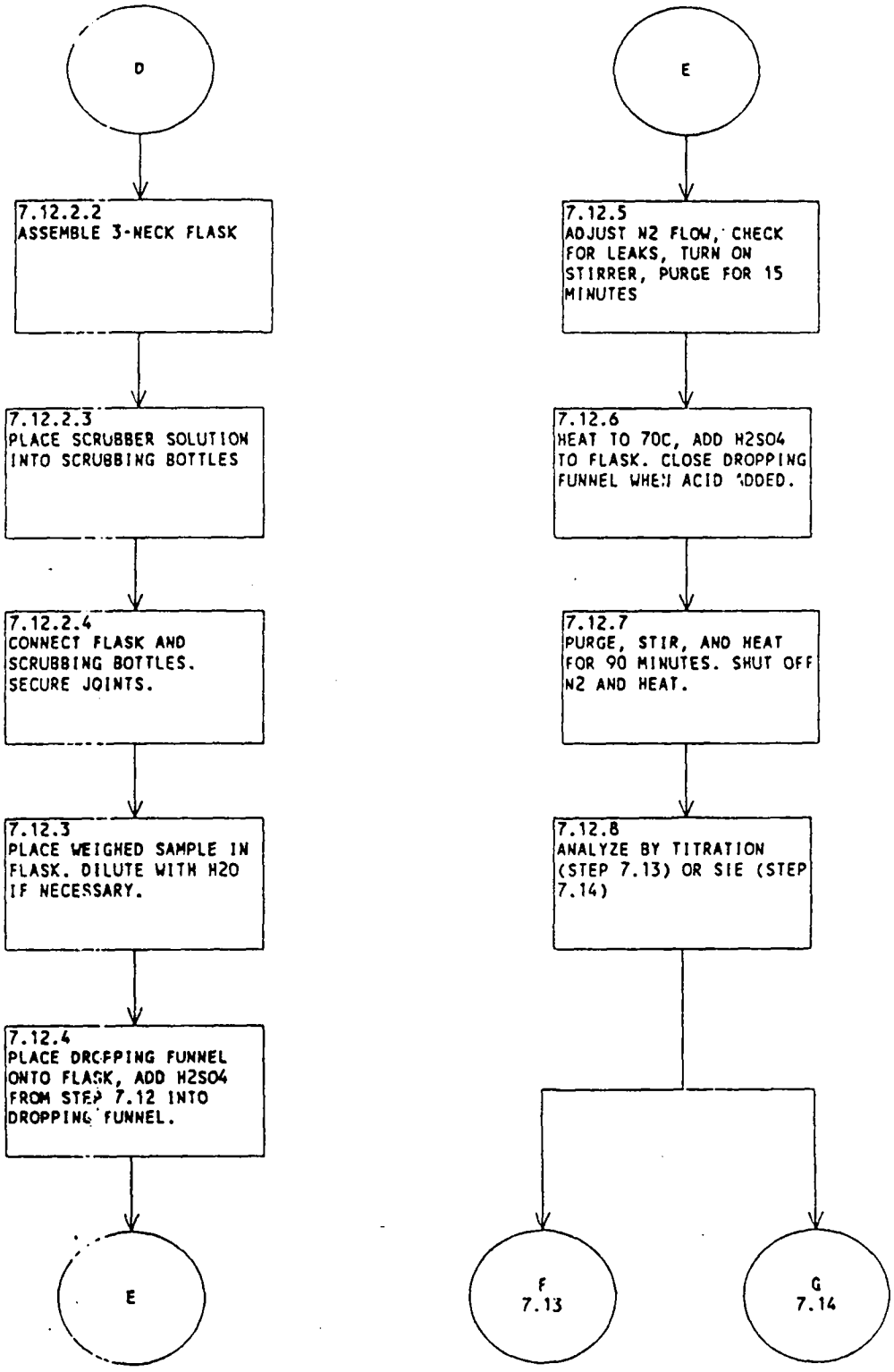
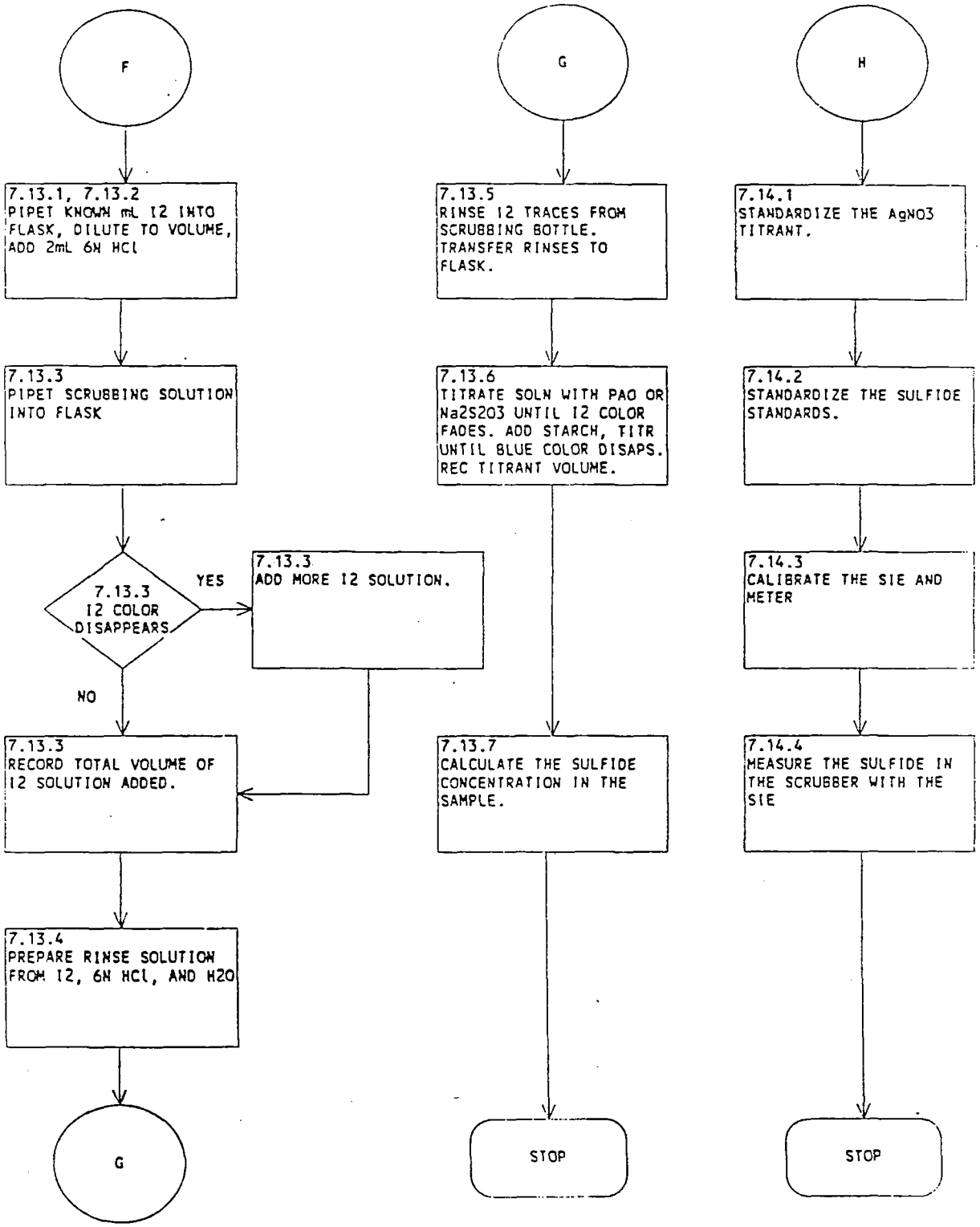


Figure 3.


START
7.1
ASSEMBLE FUNNEL APP, INS. GLASS WOOL, WET WITH MEAS. VOL H2O
7.2
TRANSFER SAMPLE (1-50MG SULFIDE) TO FUNNEL, FILTER UNTIL NO FREE WATER REMAINS IN FUNNEL.
7.3
TRANSFER SOLID AND GLASS WOOL TO DRIED TARED WEIGHING DISH
7.3
OIL PHASE IN FILTRATE ?
7.3
TRANSFER FILTRATE TO SEP. FUNNEL, COLLECT AQUEOUS PHASE, MEAS. VOL., TRANSFER OIL PHASE TO WEIGHING DISH
7.4
WEIGH DISH AND CONTENTS, SUB. GLASS FIBER (IF ANY), SU. TOTAL RINSE VOL. FROM FILTRATE VOL.
A
A
7.5
PLACE IN 1L BOTTLE: 500mL H2O, 5mL 50%NaOH, 1G SnCl2, 50mL HEXANE (IF OIL OR GREASE PRESENT)
7.5
CAP BOTTLE AND SHAKE, SPARGE BOTTLE WITH N2 TO PURGE O2
7.5
SOLIDS>25G
7.5
WEIGH OUT 25G, ADD TO BOTTLE WHILE PURGING
7.5
ADD ALL SOLIDS, CAP BOTTLE
7.6
pH OF EXTRACT MUST BE >9 <11. SHAKE BOTTLE 1 MIN, OPEN UNDER N2, CHECK pH
B


B
7.6
IS pH>9
?
YES
7.6
ADD 5mL ALIQUOT 50% NaOH UNTIL pH>9, PURGE O2, RECAP BOTTLES, REPEAT IF NECESSARY
NO
7.7
PLACE BOTTLE IN TUMBLER, TURN ON AND RUN FOR 18 HOURS.
7.8
PREPARE FUNNEL AS IN STEP 7.1
7.9
DECANT EXTRACT INTO FUNNEL
7.10
OIL PHASE IN EXTRACT
?
YES
7.10
PLACE EXTRACT IN SEP. FUNNEL, COLLECT AND MEASURE VOLUME OF AQUEOUS PHASE
NO
C
C
7.11
COMBINE AQUEOUS EXTRACT AND SAMPLE FILTRATE IN ALIQUOTS PROPORTIONAL TO THE ORIGINAL SAMPLE
7.12.1
CHOOSE SAMPLE SIZE (1-50MG SULFIDE), PLACE IN BEAKER, ADD H2O, ADD H2SO4 UNTIL pH<=1
7.12.1
CALCULATE mL H2SO4 REQUIRED TO ACIDIFY SAMPLE
7.12.2
PREPARE GAS EVOLUTION APPARATUS (SEE FIGURE 1)
7.12.2.1
PREPARE HOT WATER BATH
D


D
7.12.2.2
ASSEMBLE 3-NECK FLASK
7.12.2.3
PLACE SCRUBBER SOLUTION INTO SCRUBBING BOTTLES
7.12.2.4
CONNECT FLASK AND SCRUBBING BOTTLES. SECURE JOINTS.
7.12.3
PLACE WEIGHED SAMPLE IN FLASK. DILUTE WITH H2O IF NECESSARY.
7.12.4
PLACE DROPPING FUNNEL ONTO FLASK, ADD H2SO4 FROM STEP 7.12 INTO DROPPING FUNNEL.
E
E
7.12.5
ADJUST N2 FLOW, CHECK FOR LEAKS, TURN ON STIRRER, PURGE FOR 15 MINUTES
7.12.6
HEAT TO 70C, ADD H2SO4 TO FLASK. CLOSE DROPPING FUNNEL WHEN ACID ADDED.
7.12.7
PURGE, STIR, AND HEAT FOR 90 MINUTES. SHUT OFF N2 AND HEAT.
7.12.8
ANALYZE BY TITRATION (STEP 7.13) OR SIE (STEP 7.14)
F
7.13
G
7.14


F
7.13.1, 7.13.2
PIPET KNOWN mL I2 INTO FLASK, DILUTE TO VOLUME, ADD 2mL 6N HCl
7.13.3
PIPET SCRUBBING SOLUTION INTO FLASK
7.13.3
I2 COLOR DISAPPEARS
YES
7.13.3
ADD MORE I2 SOLUTION.
NO
7.13.3
RECORD TOTAL VOLUME OF I2 SOLUTION ADDED.
7.13.4
PREPARE RINSE SOLUTION FROM I2, 6N HCl, AND H2O
G
G
7.13.5
RINSE I2 TRACES FROM SCRUBBING BOTTLE. TRANSFER RINSES TO FLASK.
7.13.6
TITRATE SOLN WITH PAO OR Na2S2O3 UNTIL I2 COLOR FADES. ADD STARCH, TITR UNTIL BLUE COLOR DISAPS. REC TITRANT VOLUME.
7.13.7
CALCULATE THE SULFIDE CONCENTRATION IN THE SAMPLE.
STOP
H
7.14.1
STANDARDIZE THE AgNO3 TITRANT.
7.14.2
STANDARDIZE THE SULFIDE STANDARDS.
7.14.3
CALIBRATE THE SIE AND METER
7.14.4
MEASURE THE SULFIDE IN THE SCRUBBER WITH THE SIE
STOP

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16. ABSTRACT

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 is 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.

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