

METHOD 9031

EXTRACTABLE 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. Specifically, this method is designed for the extraction of soluble sulfides. This method is applicable to oil, solid, multiphase, and all other matrices not amenable to analysis by Method 9030. This method is not applicable for reactive sulfide. Refer to Chapter Seven for the determination of reactive sulfide.

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 may be filtered and the solids extracted with water at pH > 9 and < 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 (H₂S) which is formed is distilled under acidic conditions and carried by a nitrogen stream into zinc acetate gas scrubbing bottles where it is precipitated as zinc sulfide.

2.2 The sulfide in the zinc sulfide precipitate is oxidized to sulfur with a known amount of excess iodine. Then the excess iodine is determined 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.

3.0 INTERFERENCES

3.1 Samples with aqueous layers 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 values. 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 method shows no sensitivity to sulfite or hydrosulfite at concentrations up to 10 mg/kg of the interferent.

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

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

4.0 APPARATUS AND MATERIALS

4.1 Extractor - Any suitable device that sufficiently agitates a sealed container of one liter volume or greater. For the purpose of this analysis, agitation is sufficient when:

1. All sample surfaces are continuously brought into contact with extraction fluid, and
2. 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 μm 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 Gas Evolution 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 outlet - 24/40 joint reduced to 1/4 inch tube.

4.3.5 Gas scrubbing bottles - 125-mL, with 1/4 in. o.d. inlet and outlet tubes. Impinger tube must not be fritted.

4.3.6 Tubing - 1/4 in. o.d. Teflon or polypropylene. Do not use rubber.

4.4 Hot plate stirrer.

- 4.5 pH meter.
- 4.6 Nitrogen regulator.
- 4.7 Flowmeter.
- 4.8 Separatory funnels - 500-mL.
- 4.9 Tumbler - See Figures 2 and 3.
- 4.10 Top-loading balance - capable of weighing 0.1 g.

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 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Zinc acetate (for sample preservation) (2N), $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$. Dissolve 220 g of zinc acetate dihydrate in 500 mL of water.

5.4 Sodium hydroxide (50% w/v in water), NaOH. Commercially available.

5.5 Tin (II) chloride, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, granular.

5.6 n-Hexane, C_6H_{14} .

5.7 Nitrogen, N_2 .

5.8 Sulfuric acid (concentrated), H_2SO_4 .

5.9 Zinc acetate for the scrubber (approximately 0.5M). Dissolve 110 g zinc acetate dihydrate in 200 mL of water. Add 1 mL concentrated hydrochloric acid, HCl, to prevent precipitation of zinc hydroxide. Dilute to 1 liter.

5.10 Formaldehyde (37% solution), CH_2O . Commercially available.

5.11 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, $\text{C}_7\text{H}_6\text{O}_3$, as a preservative, in 100 mL hot water.

5.12 Iodine solution (approximately 0.025N). Dissolve 25 g of potassium iodide, KI, in 700 mL of water in a 1-liter volumetric flask. Add 3.2 g of iodine, I_2 . 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 standard phenylarsine oxide, or 0.025N sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, until the amber color fades. Add starch indicator solution until the solution turns

deep blue. Continue titration drop by drop until the blue color disappears. Run in replicate. Calculate the normality as follows:

$$\text{Normality (I}_2\text{)} = \frac{\text{mL of titrant} \times \text{normality of titrant}}{\text{Volume of sample (mL)}}$$

5.13 Sodium sulfide nonahydrate $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$, for the preparation of standard solutions to be used for calibration curves. Standards must be prepared at $\text{pH} > 9$ and < 11 .

5.14 Titrant.

5.14.1 Standard phenylarsine oxide (PAO) solution (0.025N), $\text{C}_6\text{H}_5\text{AsO}$. This solution is commercially available.

CAUTION: PAO is toxic.

5.14.2 Standard sodium thiosulfate solution (0.025N), $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. Dissolve 6.205 ± 0.005 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in 500 mL of water. Add 9 mL 1N NaOH and dilute to 1 liter.

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 this manual.

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 aqueous or multiphasic sample. Adjust the pH to greater than 9.0 with 50% NaOH. Fill the sample bottle completely and stopper with a minimum of aeration. For solid samples, fill the surface of 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 Weigh 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% w/v NaOH
1 g $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$
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% 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 a 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:

$$\frac{\text{Aliquot of the Filtrate(mL)}}{\text{Aliquot of the Extract(mL)}} = \frac{\text{Solid Extracted(g)}^a}{\text{Total Solid(g)}^b} \times \frac{\text{Total Sample Filtrate(mL)}^c}{\text{Total Extraction Fluid(mL)}^d}$$

^aFrom Step 7.5. Weight of solid sample used for extraction.

^bFrom Step 7.4. Weight of solids and oil phase with the dry weight of filter and tared dish subtracted.

^cIncludes volume of all rinses added to the filtrate (Steps 7.1 and 7.2).

^d500 mL water plus total volume of NaOH solution. Does not include hexane, which is subsequently removed (Step 7.10).

Alternatively, the samples may be distilled and 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 1.0 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 hotplate 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 Place into each gas scrubbing bottle 10 ± 0.5 mL of the 0.5M zinc acetate solution, 5.0 ± 0.1 mL of 37% formaldehyde and 100 ± 5.0 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 1.0 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 7.1.1 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 a rate of 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 the magnetic stirrer. Purge the 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 contained 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 5.12) 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 to the iodine.

7.13.3 Pipet both of the gas scrubbing bottle solutions into 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 7.13.1 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.

7.13.7 Calculate the concentration of sulfide in the sample as follows:

$$\frac{[(\text{mL of I}_2 \times \text{N of I}_2) - (\text{mL of titrant} \times \text{N of titrant})](16.03)}{\text{sample weight (kg)}} = \text{sulfide(mg/kg)}$$

8.0 QUALITY CONTROL

8.1 All quality control data must be maintained and available for reference or inspection for a period of three 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 every twenty 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 every twenty samples. Acceptable recovery will depend on the level and matrix.

8.4 A matrix spiked sample should be run for each analytical batch or twenty samples, whichever is more frequent, to determine matrix effects. If recovery is low, acid-insoluble sulfides are indicated. A matrix spiked 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 twenty samples or once per analytical batch, whichever is more frequent.

9.0 METHOD PERFORMANCE

9.1 Accuracy - Accuracy for this method was determined by three independent laboratories by measuring percent recoveries of spikes for waste samples. The results are summarized below.

Accuracy for the entire method for four synthetic waste samples 70-104% recovery

9.2 Precision

Precision of entire method for four synthetic waste samples
Percent coefficient of variation 1.0-34

10.0 REFERENCES

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FIGURE 1.
GAS EVOLUTION APPARATUS

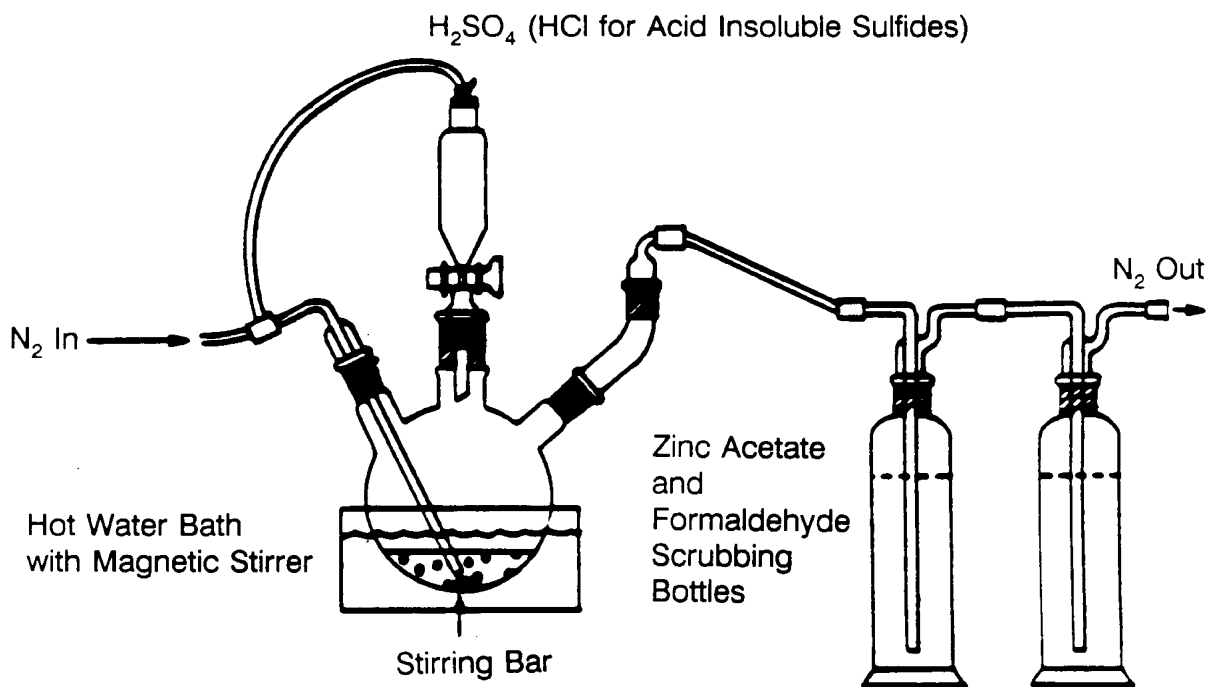


FIGURE 2.
TUMBLER-EXTRACTOR

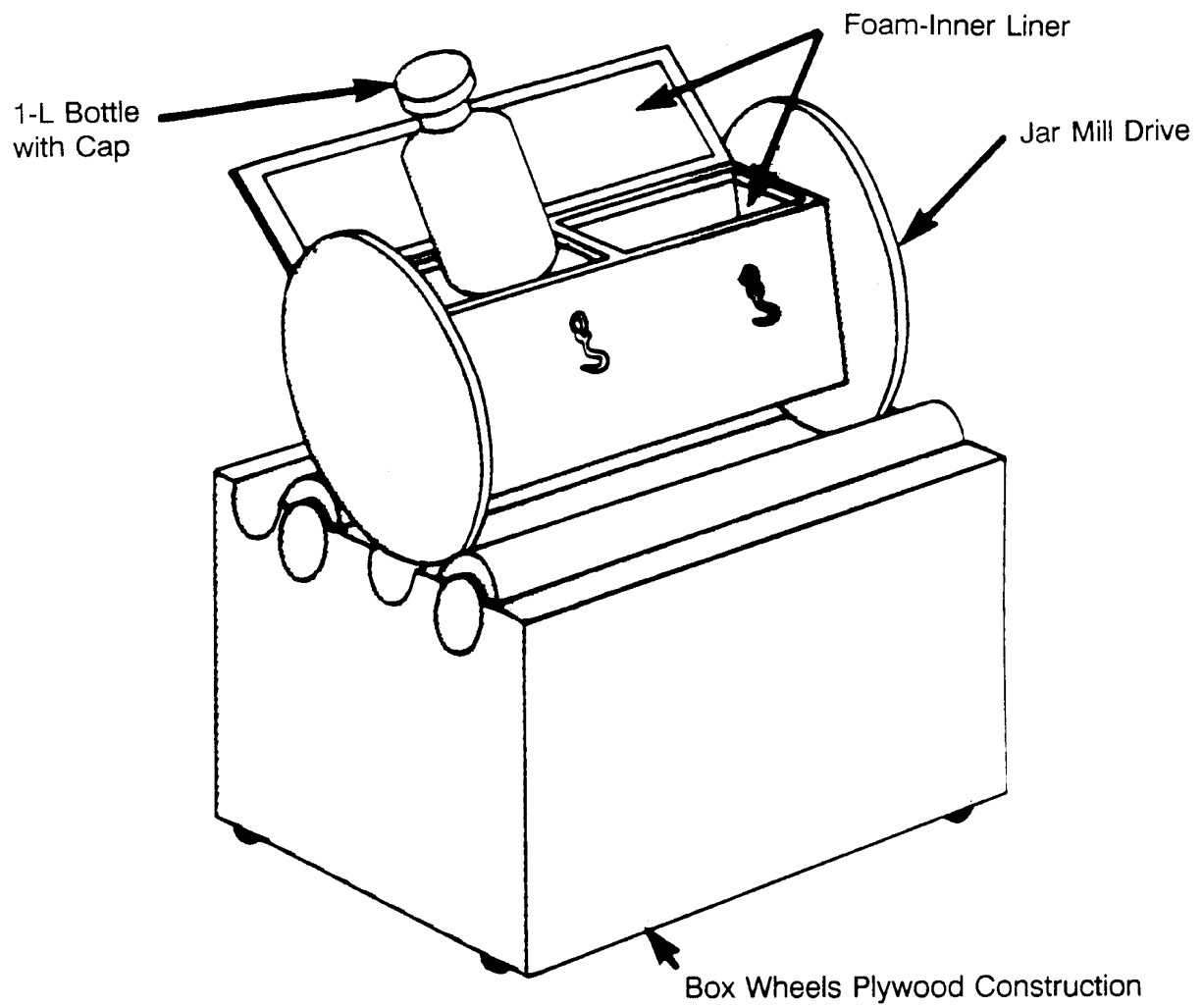
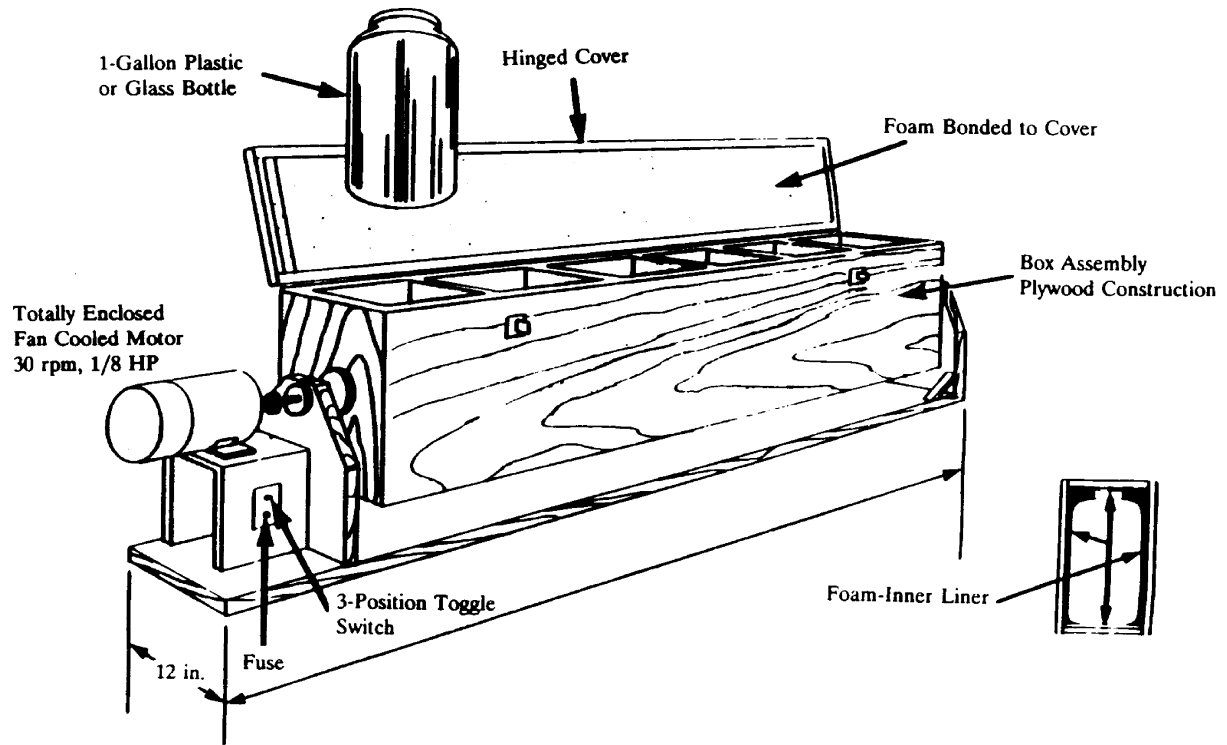
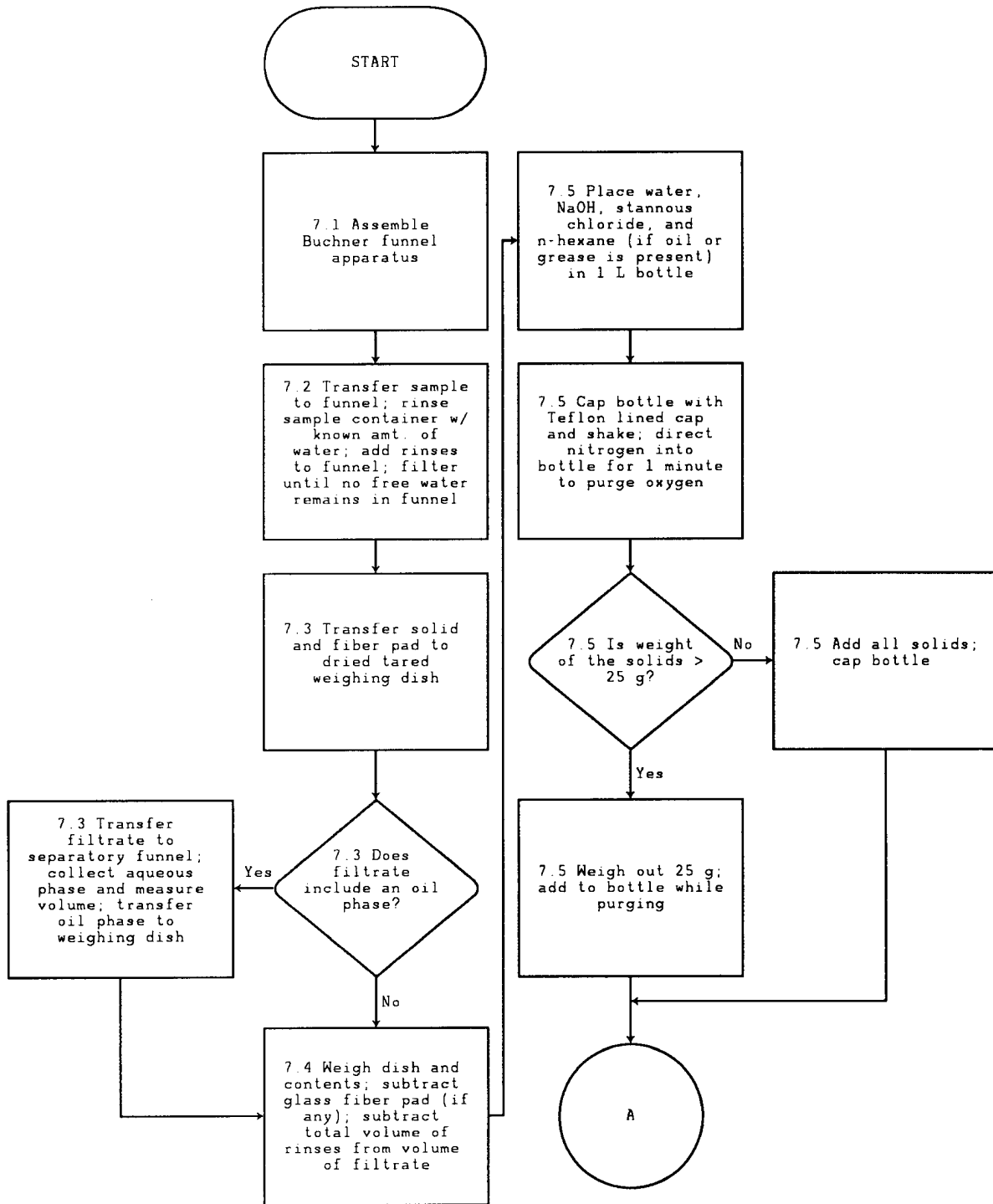


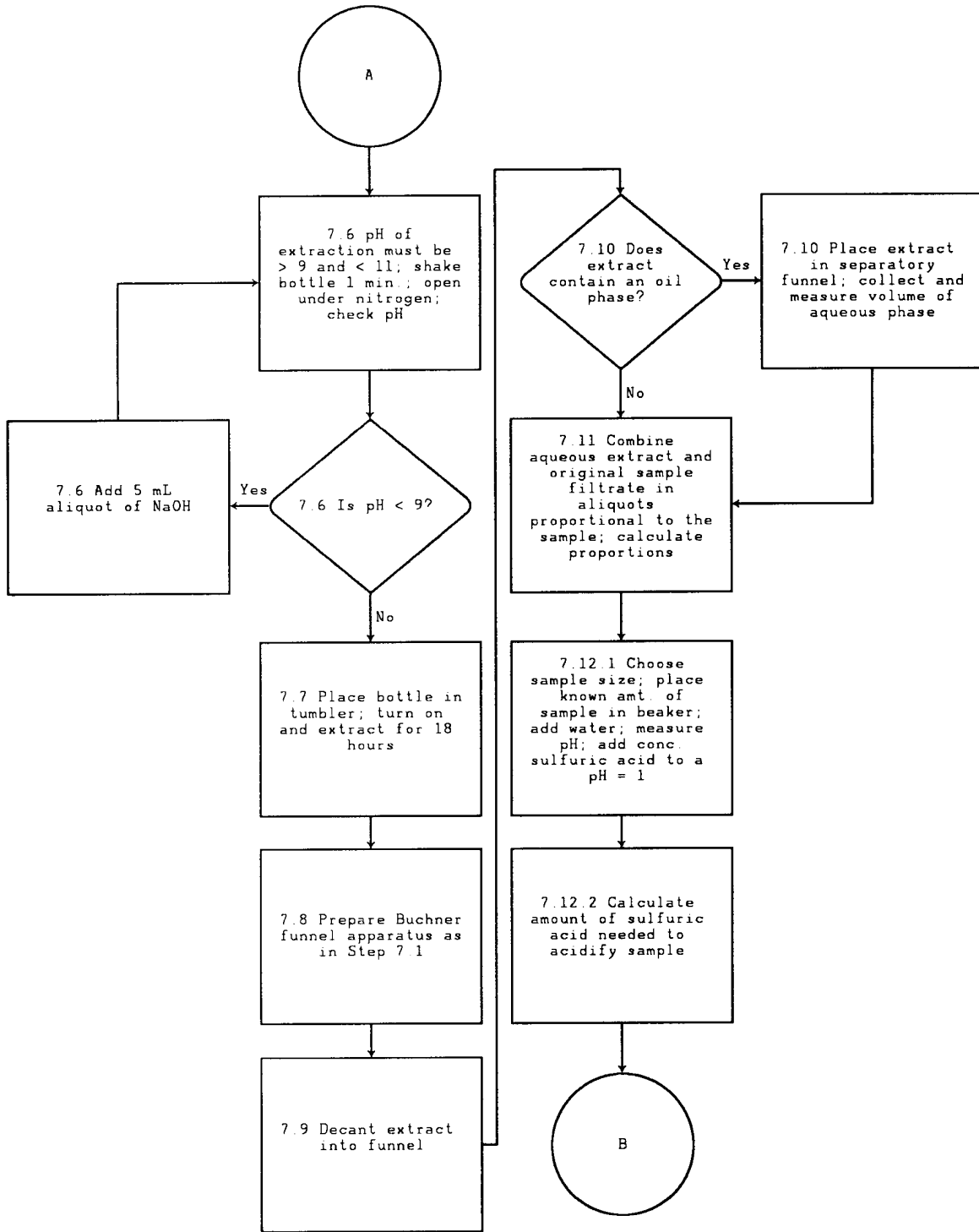
FIGURE 3.
EXTRACTOR



METHOD 9031
SULFIDES



METHOD 9031
(Continued)



METHOD 9031
(Continued)

