State of California
Air Resources Board

Method 426

Determination of Cyanide Emissions from Stationary Sources

Adopted: January 22, 1987

Method 426 - Determination of Cyanide Emissions from Stationary Sources

1. APPLICABILITY AND PRINCIPLE

1.1 Applicability

This method is for determination of cyanides in aerosol and gas emissions from stationary sources. Cyanide is defined as cyanide ion and complex cyanide converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

1.2 Principle

Particulate and gaseous emissions are extracted isokinetically from the stack and passed through an impinger-filter train where the cyanide is collected on a glass-fiber filter and in a solution of sodium hydroxide. The combined filter extract and impinger solution are analyzed for cyanide by either titrating with standard silver nitrate in the presence of a silver sensitive indicator or by colorimetric procedure using Chloramine-T with either pyridine-barbituric acid or pyridine-pyrazolone color forming reagents.

2. RANGE AND SENSITIVITY

The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide greater than 1 mg/L (0.25 mg/250 mL of absorbing liquid). The detection limit for this procedure is 0.3 mg/L.

The colormetric procedure has an optimum working range of 0.02 - 1 mg/L, and a detection limit of 0.01 mg/L.

3. INTERFERENCES

Sulfides adversely affect the colorimetric and titration procedures. Samples that contain hydrogen sulfide, metal sulfides or other compounds that may produce hydrogen sulfide during the distillation should be distilled by the procedure described in Section 6.3.3.2. The apparatus for this procedure is shown in Figure 3.

Positive errors may occur with samples that contain nitrite and/or nitrate. During the distillation, nitrite and nitrate form nitrous acid which reacts with some organic compounds to form oximes. These compounds will decompose under test conditions to generate HCN. The interference of nitrite and nitrate is eliminated by pretreatment with sulfamic acid.

Since oxidizing agents may decompose most of the cyanides, they must be removed during sample recovery (Section 6.2.1.1).

If the analytical method herein recommended does not give the desired sensitivity in the presence of interfering substances in the sample, the tester may select an equivalent procedure, subject to the approval of the Executive Officer. The tester must then produce data to demonstrate that the method is equivalent, and substantiate this data through an adequate quality assurance program approved by the Executive Officer.

4. APPARATUS

The following sampling apparatus is recommended. The tester may use an alternative sampling apparatus only if, after review by the Executive Officer, it is deemed equivalent for the purposes of the method.

4.1 Sampling Train

A schematic diagram of the sampling train is shown in Figure 1. This is similar to the CARB Method 5 sampling train with some minor changes which are described below.

4.1.1 Probe Nozzle, Probe Liner, Pitot Tube, Differential Pressure Gauge, Filter Holder, Filter Heating System, Metering System, Barometer and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.1 to 2.1.6, and 2.1.8 to 2.1.10, respectively.

4.1.2 Impingers. Four impingers are connected in series with glass ball joint fittings. The first, third, and fourth impingers are of the Greenburg-Smith design modified by replacing the tip with a 1-cm (0.5 in.) I.D. glass tube extending to 1 cm from the bottom of the flask. The second impinger is of the Greenburg-Smith design with the standard tip.

The first and second impingers shall contain known quantities of 0.1 N NaOH (Section 6.1.3). The third shall be empty, and the fourth shall contain a known weight of silica gel or equivalent desiccant.

In the case of sources which produce significant levels of carbon dioxide, the tester may substitute sodium bicarbonate for sodium hydroxide in the first and second impingers.

A thermometer which measures temperatures to within 1^{o} C (2^{o} F), should be placed at the outlet of the fourth impinger.

4.2 Sample Recovery.
The following items are needed:

4.2.1 Probe Liner and Probe Nozzle Brushes, Petri Dishes, Plastic Storage Containers, Rubber Policeman and Funnel. Same as Method 5, Sections 2.2.1, 2.2.4, 2.2.6 and 2.2.7, respectively.

4.2.2 Wash Bottles. Glass (2)

4.2.3 Sample Storage Containers. Alkali resistant polyethylene bottles. Impinger and probe solutions and washes, 1000 mL. Use screw-cap liners that are either rubber-backed Teflon or leak-free and resistant to attack by alkali.

4.2.4 Graduated Cylinder and/or Balance. To measure the volume of condensed water to within 2 mL, or the weight to within 1 g. Use a graduated cylinder that has a minimum capacity of 500 mL, and subdivisions no greater than 2 mL. (Most laboratory balances are capable of weighing to the nearest 0.5 g or less).

4.2.5 Funnel. Glass, to aid in sample recovery.

4.3 Analysis.
The following equipment is needed:

4.3.1 Reflux distillation apparatus assembled as shown in Figure 1 or Figure 2. The boiling flask should be of 1 liter size with inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

4.3.2 Microburet. 5.0 mL (for titration).

4.3.3 Spectrophotometer suitable for measurements at 578 nm or 620 nm with a 1.0 cm cell or larger.

4.3.4 Reflux distillation apparatus for sulfide removal as shown in Figure 3. The boiling flask should be of 1-liter size with inlet tube and provision for condenser as in 4.3.1. The sulfide scrubber may be a Wheaton Bubbler #709682 with 29/42 joints, size 100

mL. The air inlet tube should not be fritted. The cyanide absorption vessel should be the same as the sulfide scrubber. The air inlet tube of this absorber should be fritted.

4.3.5 Flow Meter. Such as Lab Crest with stainless steel float (Fisher 11-164-50).

4.3.6 Erlenmeyer Flasks. 125-mL. 24/40 Standard Taper.

4.3.7 Whatman No. 42 filter paper (or equivalent).

4.3.8 Volumetric Flasks. 100-mL, 250-mL and 1000-mL.

4.3.9 Balance - Analytical. Capable of accurately weighing to the nearest 0.0001 g.

5. REAGENTS

Unless otherwise specified, use ACS reagent grade chemicals or equivalent.

Mention of trade names or specific products does not constitute endorsement by the California Air Resources Board.

5.1 Sampling.
The following reagents are needed:

5.1.1 Glass Fiber Filters, Silica Gel, Crushed Ice and Stopcock Grease. Same as Method 5, Sections 3.1.1, 3.1.2, 3.1.4 and 3.1.5, respectively.

5.1.2 Water. Deionized, distilled, to conform to ASTM Specification D1193-77, Type 3. If high concentrations of organic matter are not expected to be present, the analyst may omit the potassium permanganate test for oxidizable organic matter.

5.1.3 Sodium Hydroxide Solution, 0.1 N. Dissolve 4.0 g NaOH in deionized distilled water, and dilute to 1 liter with water.

5.2 Sample Recovery.

5.2.1 Sodium Hydroxide Solution, 0.1 N. Same as 5.1.3 above.

5.2.2 Sodium Hydroxide Solution, 10 N. Dissolve 40 g NaOH in

deionized distilled water, and dilute to 100 mL.

5.2.3 Ascorbic acid, crystals.

5.2.4 Potassium iodide-starch test paper (KI-starch paper).

5.3 Analysis.
The following reagents are needed:

5.3.1 Water. Same as 5.1.2 above.

5.3.2 Sodium Hydroxide Solution, 1.25 N. Dissolve 50 g of NaOH in deionized distilled water, and dilute to 1 liter.

5.3.3 Dilute Sodium Hydroxide Solution, 0.25 N. Dilute 200 mL of 1.25 N sodium hydroxide solution (5.3.2) to 1000 mL with deionized distilled water.

5.3.4 Sulfuric Acid, 18 N. Slowly add 500 mL of concentrated H_2SO_4 to 500 mL deionized distilled water.

5.3.5 Sodium Dihydrogenphosphate, 1M. Dissolve 138 g of $NaH_2PO_4.H_2O$ in 1 liter of deionized distilled water. Refrigerate this solution.

5.3.6 Standard silver nitrate solution, 0.0192 N. Prepare by crushing approximately 5 g $AgNO_3$ crystals and drying to constant weight at 40^o C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in deionized distilled water, and dilute to 1000 mL (1 mL = 1 mg CN^-).

5.3.7 Stock Cyanide Solution. Dissolve 2.51 g of KCN and 2 g of KOH in 900 mL of deionized distilled water. Standardize with 0.0192 N $AgNO_3$ (Section 5.3.6). Dilute to appropriate concentration so that 1 mL = 1 mg CN^-.

5.3.8 Intermediate standard cyanide solution. Dilute 100.0 mL of stock cyanide solution (1 mL = 1 mg CN^-) to 1000 mL with deionized distilled water. (1 mL = 100.0 ug CN^-).

5.3.9 Working standard cyanide solution. Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1000 mL with distilled water and store in a glass stoppered bottle (1 mL =

10.0 ug CN^-).

5.3.10 Cyanide Calibration Standards. Pipet 0.0, 1.0, 2.0, 5.0, 10.0, 15.0 and 20.0 mL of the working cyanide standard solution (5.3.9) into 250-mL volumetric flasks. To each flask, add 50 mL of 1.25 N sodium hydroxide, and dilute to 250 mL with deionized distilled water. These working standards contain 0.0, 0.04, 0.08, 0.20, 0.40, 0.60 and 0.80 mg CN^-/L, respectively. Prepare as needed, additional standards at other concentrations in a similar manner.

5.3.11 Rhodanine indicator. Dissolve 20 mg of p-dimethyl-amino-benzalrhodanine in 100 mL of acetone.

5.3.12 Chloramine-T solution. Dissolve 1.0 g of white, water-soluble Chloramine-T in 100 mL of deionized distilled water and refrigerate until ready to use. Prepare fresh daily.

5.3.13 Color Reagent - One of the following may be used:

5.3.13.1 Pryidine-Barbituric Acid Reagent. Place 15 g of barbituric acid in a 250 mL volumetric flask and add just enough distilled water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of conc. HCl, mix, and cool to room temperature. Dilute to 250 mL with deionized distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

5.3.13.2 Pyridine-pyrazolone solution.

(a) 3-Methyl-l-phenyl-2-pyrazolin-5-one reagent, saturated solution. Add 0.25 g of 3-methyl-1-phenyl-2-pyrazolin-5-one to 50 mL of distilled water, and heat to 60^o C with stirring. Cool to room temperature.

NOTE: It is imperative that this synthesis be performed as directed.

(b) 3,3'Dimethyl-1, 1'-diphenyl-[4,4'-bi-2 pyrazoline]-5,5'dione (bispyrazolone): Dissolve

0.01 g of bispyrazolone in 10 mL of pyridine.

(c) Pour solution (5.3.13.2a) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (5.3.13.2b) collecting the filtrate in the same container as filtrate from (5.3.13.2a). Mix until the filtrates are homogeneous. The mixed reagent develops a pink color but this does not affect the color production with cyanide if used within 24 hours of preparation.

5.3.14 Magnesium chloride solution. Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000 mL flask. Dissolve and dilute to 1 liter with deionized distilled water.

5.3.15 Lead acetate. Dissolve 30 g of $Pb(C_2H_3O_2) \cdot 3H_2O$ in 950 mL of deionized distilled water. Adjust the pH to 4.5 with acetic acid. Dilute to 1 liter.

5.3.16 Sulfamic acid.

6. PROCEDURE

6.1 Sampling.
Because of the complexity of this method, testers should be trained and experienced with the test procedures in order to ensure reliable results.

6.1.1 Pretest Preparation. Follow the same general procedure described in Method 5, Section 4.1.1, except the filter need not be weighed.

6.1.2 Preliminary Determinations. Follow the same general procedure described in Method 5, Section 4.1.2.

6.1.3 Preparation of Collection Train. Follow the same general procedure given in Method 5, Section 4.1.3, except place 100 mL of 0.1 N NaOH in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. Assemble the train as shown in CARB Method 5, Figure 5-1.

6.1.4 Leak-Check Procedures. Follow the general leak-check

procedures given in Method 5, Sections 4.1.4.1 (Pretest Leak-Check), 4.1.4.2 (Leak-Checks During the Sample Run), and 4.1.4.3 (Post-Test Leak-Check).

6.1.5 Sampling Train Operation. Follow the same general procedure given in Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in CARB Method 5, Figure 5-2.

6.1.6 Calculation of Percent Isokinetic. Same as Method 5, Section 4.1.6.

6.2 Sample Recovery.
Begin proper clean-up procedure as soon as the probe is removed from the stack at the end of the sampling period.

Allow the probe to cool. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it. Do not cap off the probe tip tightly while the sampling train is cooling, as this would create a vacuum in the filter holder, thus drawing liquid from the impingers into the filter.

Before moving the sampling train to the cleanup site, remove the probe from the sampling train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the glassware inlet where the probe was fastened and cap the inlet. Remove the umbilical cord from the last impinger and cap the impinger. The tester may use ground-glass stoppers, plastic caps, or serum caps to close these openings.

Transfer the probe and filter-impinger assembly to a cleanup area, which is clean and protected from the wind so that the chances of contaminating or losing the sample are minimized.

Inspect the train prior to and during disassembly and note any abnormal conditions.

Check the pH of the impinger solutions to ascertain that the pH is still basic, and that the test was a valid one.

Treat the samples as follows:

6.2.1 Container No. 1 (Filter). Carefully remove the filter from the filter

holder and place it in a glass sample container containing 50 mL of 0.1 N NaOH. Carefully transfer any visible particulate matter and/or filter fibers that adhere to the filter holder gasket with a dry Nylon bristle brush and/or sharp-edged blade.

6.2.1.1 Oxidising agents. If oxidising agents are known or suspected to be present, test and treat the sample as follows. Test a drop of the sample with potassium iodide-starch test paper (KI-starch paper). A blue color indicates the need for treatment. Add ascorbic acid, few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

6.2.1.2 Preservation. Samples must be preserved with 2 mL 10 N sodium hydroxide (5.3.2) per liter of sample (pH ≥ 12) at the time of collection.

6.2.2 Container No. 2 (Probe). Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, clean all surfaces that have been exposed to the sample (including the probe nozzle, probe fitting, probe liner, and front half of the filter holder) with 0.1 N NaOH. Place the wash in a glass sample storage container. Measure and record (to the nearest 2-mL) the total amount of 0.1 N NaOH used for each rinse. Perform the rinses with 0.1 N NaOH as follows:

Carefully remove the probe nozzle and rinse the inside surface with 0.1 N NaOH from a wash bottle. Brush with a Nylon-bristle brush, and rinse until the rinse shows no visible particles, after which, make a final rinse of the inside surface. Brush and rinse the inside parts of the Swagelok fitting with 0.1 N NaOH in a like manner until no visible particles remain.

Rinse the probe liner with 0.1 N NaOH. While squirting the sodium hydroxide rinse into the upper end of the probe, tilt and rotate the probe so that all inside surfaces will be wetted with the 0.1 N NaOH. Let the 0.1 N NaOH drain from the lower end into the sample container. The tester may use a glass funnel to aid in transferring liquid washes to the container. Follow the rinse with a probe brush. Hold the probe in an inclined position, and squirt 0.1 N NaOH into the upper end as the probe brush is

being pushed with a twisting action through the probe. Hold the sample container underneath the lower end of the probe, and catch any liquid and particulate matter brushed from the probe. Run the brush through the probe three times or more until no visible sample matter is carried out with the 0.1 N NaOH and none remains on the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times, since metal probes have small crevices in which particulate matter can be entrapped. Rinse the brush with 0.1 N NaOH and quantitatively collect these washings in the sample container. After the brushing, make a final rinse of the probe as described above. It is recommended that two people clean the probe to minimize loss of sample: Between sampling runs, keep brushes clean and protected from contamination.

After ensuring that all joints have been wiped clean of silicone grease, brush and rinse with 0.1 N NaOH the inside of the front half of the filter holder. Brush and rinse each surface three times or more, if needed, to remove visible particulate matter. Make a final rinse of the brush and filter holder.

After all washings have been collected in the sample container, test a drop of the sample with potassium iodide-starch test paper (KI-starch paper). A blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each litre of sample volume.

Samples must be preserved with 2 mL 10 N sodium hydroxide per liter of sample (pH ≥ 12) at the time of collection.

Tighten the lid on the sample container so that the fluid will not leak out when it is transported to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during shipment. Label the container to clearly identify its contents.

Rinse the glassware a final time with water to remove residual NaOH before reassembling. Do not save the final rinse water.

Repeat the test for oxidising agents (6.2.1.1) and then preserve the sample (6.2.1.2).

6.2.3 Container No. 3 (Silica Gel). Check the color of the indicating silica gel to determine if it has been completely spent, and note its condition. Transfer the silica gel from the fourth impinger to the original container and seal. The tester may use a funnel to pour the silica gel and rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of particles that may adhere to the impinger walls and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, the tester may follow the procedure for Container No. 2 under Section 6.4 (Analysis).

6.2.4 Container No. 4 (Impingers). If the volume of liquid is large, the tester may place the impinger solutions in several containers. Clean each of the first three impingers and connecting glassware in the following manner:

1. Wipe the impinger ball joints free of silicone grease and cap the joints.

2. Rotate and agitate each impinger, so that the impinger contents might serve as a rinse solution.

3. Transfer the contents of the impingers to a 500-mL graduated cylinder. Remove the outlet ball joint cap and drain the contents through this opening. Do not separate the impinger parts (inner and outer tubes) while transferring their contents to the cylinder. Measure the liquid volume to within $\pm$ 2 mL. Alternatively, determine the weight of the liquid to within $\pm$ 0.5 g. Record in the log the volume or weight of the liquid present, and the occurrence of any color or film in the impinger catch. The liquid volume or weight is needed, along with the silica gel data, to calculate the stack gas moisture content (see Method 5, Figure 5-3).

   Determine the pH of the impinger solution to ascertain whether it is still basic and whether the test was a valid one.

4. Transfer the contents to Container No. 4.

5. Note: In steps 5 and 6 below, measure and record the total amount of 0.1 N NaOH used for rinsing. Pour approximately 30 mL of 0.1 N NaOH into each of the first three impingers and agitate the impingers. Drain the 0.1 N NaOH through the outlet arm of each impinger into Container No. 3. Repeat this operation a second time; inspect the impingers for any abnormal conditions.

6. Wipe the ball joints of the glassware connecting the impingers free of silicone grease and rinse each piece of glassware twice with 0.1 N NaOH; transfer this rinse into Container No. 3. (Do not rinse or brush the glass-fritted filter support). Repeat the procedure described in Section 6.2.1.1 above.

   Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to clearly identify its contents.

6.2.5 Sample Blanks (Container No. 5). Prepare a blank by placing an unused filter in a glass container, and adding a volume of recovery solution identical to the total volume in Containers No. 1, 2 and 4. Process the blank in the same manner as the sample.

6.3 Sample Preparation.

6.3.1 Container No. 1 (Filter). Cut the filter into strips and transfer the strips and all loose particulate matter into a 125-mL Erlenmeyer flask. Rinse the petri dish with 10 mL of 1.25 N NaOH to insure a quantitative transfer and add to the flask. Pipet 25 mL of 1.25 N NaOH into the flask. Cap the flask, place on a shaker and shake for at least 30 minutes at moderate speed to complete the extraction.

6.3.2 Containers No. 2 and No. 4 (Probe and Impingers). Check the liquid level in Containers No. 2 and/or No. 4 to determine whether any sample was lost during shipment. Record observations on the analysis sheet. If a noticeable amount of leakage has occurred, either void the sample or take steps, subject to approval by the Executive Officer, to adjust the final results. Combine the contents of Containers No. 2 and No. 4 with the filter extract (6.3.1) for analysis.

6.3.3 Distillation Procedure.

6.3.3.1 Samples without sulfide. Place 500 mL of the combined sample (Section 6.3.2) or an aliquot diluted to 500 mL in the 1 liter boiling flask. Pipet 50 mL of 1.25 N sodium hydroxide (5.3.2) into the absorbing tube. If the apparatus in Figure 1 is used, add distilled water until the spiral is covered. Connect the boiling flask, condenser, absorber and trap as shown in Figure 1 or Figure 2.

Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately two bubbles of air per second enter the boiling flask through the inlet tube. Proceed to Section 6.3.5.

6.3.3.2 Samples that contain sulfide. Place 500 mL of the combined sample (6.3.2) or an aliquot diluted to 500 mL in the 1-liter boiling flask. Pipet 50 mL of 1.25 N sodium hydroxide into the absorbing tube. Add 25 mL of lead acetate solution (5.3.15) to the sulfide scrubber. Connect the boiling flask, condenser, scrubber and absorber as shown in Figure 3. The flow meter is connected to the outlet tube of the cyanide absorber.

Start a stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately 1.5 liters per minute enter the boiling flask through the air inlet tube. The bubble rate may not remain constant while heat is being applied to the flask. It may be necessary to readjust the air rate occasionally. Proceed to 6.3.5.

6.3.4 If samples contain NO_3^- and/or NO_2^-, add 2 g of sulfamic acid (5.3.16) after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of H_2SO_4.

6.3.5 Slowly add 50 mL 18 N sulfuric acid (5.3.4) through the air inlet tube. Rinse the tube with deionized distilled water and allow the

airflow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride solution (5.3.13) into the air inlet and wash down with a stream of water.

Heat the solution to boiling. Reflux for one hour. Turn off the heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect the absorber and close off the vacuum source.

Drain the solution from the absorber into a 250 mL volumetric flask. Wash the absorber with deionized distilled water, and add the washings to the flask. Dilute to volume with deionized distilled water.

6.3.6 Sample Blank (Container No. 5). Treat in the same manner as the sample (Sections 6.3.3 to 6.3.5). Use the absorbance obtained for the blank to correct the sample measurement.

6.4 Analysis.

6.4.1 Colorimetric Procedure. Sample (Containers No. 1, No. 2 and No. 4.). Withdraw 50 mL or less of the solution from the 250-mL volumetric flask (Section 6.3.3.1 or 6.3.3.2) and transfer to a 100 mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25 N sodium hydroxide solution (5.3.3). Add 15.0 mL of 1 M sodium dihydrogenphosphate solution (5.3.5) and mix.

6.4.1.1 Pyridine-Barbituric Acid Method. Add 0.5 mL of chloramine T (5.3.12) and mix. See Notes 1 and 2. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (5.3.13.1) and mix. Dilute to volume with distilled water and mix again. Allow 8 minutes for color development then measure the absorbance at 578 nm in a 1 cm cell within 15 minutes. Read ug CN^-/50 mL from the calibration curve obtained in Section 7.2. If the absorbance does not fall within the range of the calibration curve, repeat the procedure using a smaller aliquot.

6.4.1.2 Pyridine-Pyrazolone method. Add 0.5 mL of chloramine T (5.3.12) and mix. See Notes 1 and 2. After 1 to 2 minutes, add 5 mL of pyradine-

pyrazolone solution (5.3.13.2) and mix. Dilute to volume with distilled water and mix again. After 40 minutes, measure the absorbance at 620 nm in a 1 cm cell. Read the concentration of the sample (ug CN^-/50 mL) from the calibration curve obtained in Section 7.2. If the absorbance of the sample does not fall within the range of the calibration curve, repeat the analysis using a smaller aliquot.

NOTE 1 Some distillates may contain compounds that have a chlorine demand. One minute after the addition of chloramine T, test for residual chlorine with KI-starch paper. If the test is negative, add an additional 0.5 mL of chloramine T. After one minute, recheck the sample.

NOTE 2 If more than 0.5 mL of chloramine T is used with the pyridine-pyrazolone color reagent, this will prevent the color from developing.

If more than 0.5 mL of chloramine-T is used with the pyridine-barbituric acid color reagent, this will accelerate the rate at which the color fades.

6.4.2 Titration Procedure. If the sample contains more than 1 mg of CN^-/L, transfer the distillate (6.3.3), or a suitable aliquot diluted to 250 mL, to a 500-mL Erlenmeyer flask. Add 10-12 drops of the benzalrhodanine indicator. Titrate with standard silver nitrate solution (5.3.6) to the first change in color from yellowish-brown to pink. Titrate the blanks using the same amount of sodium hydroxide and indicator as in the sample.

The analyst should familiarize himself with the end point of the titration and the amount of indicator to be used before actually titrating the samples. A 5- or 10-mL microburet may be used to obtain a more precise titration.

6.4.3 Sample Blank (Container No. 5). Follow the same procedure used for the sample (Section 6.4.1 or 6.4.2 above). Use the same aliquot size as that used for the sample.

6.4.4 Container No. 3 (Silica Gel). The tester may conduct this step in the field. Weigh the spent silica gel (or silica gel plus impinger)

to the nearest 0.5 g; record this weight.

7. CALIBRATION.

7.1 Sampling Train Calibration.
Calibrate the sampling train components according to the following sections of Method 5: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Probe Heater (Section 5.4); Temperature Gauges (Section 5.5); Leak-Check of the Metering System (Section 5.6); and Barometer (Section 5.7).

7.2 Spectrophotometer.
Pipet 50 mL of each calibration standard (5.3.10) into a 100-mL volumetric flask, and treat according to Section 6.4.1. These standards will contain 0.0, 2.0, 4.0, 10.0, 20.0, 30.0 and 40.0 ug CN^-/50 mL.

With the spectrophotometer at 620 nm for pyridine-pyrazolone, or 578 nm for pyridine-barbituric acid, use the reagent blank (7.2) to set the absorbance to zero. Determine the absorbance of the standards, and plot net absorbance versus ug CN^-/50 mL. Draw a smooth curve through the points. The curve should pass through the origin.

7.2.1 Samples without sulfide. It is not imperative that all standards be distilled in the same manner as the samples. However, it is recommended that at least two standards (a high and low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within $\pm$10% of the undistilled standards, the operator should find the cause of the apparent error before proceeding.

7.2.2 Samples that contain sulfide. It is imperative that all standards be distilled in the same manner as the samples. Standards distilled by this method will give a linear curve, but as the concentration increases, the recovery decreases. It is recommended that at least 3 standards be distilled.

7.3 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (5.3.8) or the working standard (5.3.9) to 500 mL of sample to insure a level of 20 ug/L. Proceed with the analysis as in Section 6.3.3.

8. CALCULATIONS.

8.1 Nomenclature

A_t = Aliquot of total sample added to the still, mL (6.3.3)

A_d = Aliquot of distillate taken for color development, mL (6.4.1).

C_c = ug CN^- from the calibration curve

V_d = Volume of distillate after dilution, mL (6.3.3)

V_t = Total volume of cyanide sample after final dilution, mL (6.3.2)

m_t = Total cyanide in sample, mg

C_s = Concentration of cyanide in the stack gas, mg/m^3, dry basis, corrected to standard conditions of 760 mm Hg (29.92 in. Hg) and 293^o K (528^o R).

Q_t = Aliquot of sample used for titration, mL

T = Volume of $AgNO_3$ for titration of sample, mL

B = Volume of $AgNO_3$ for titration of blank, mL

8.2 Dry Gas Volume.
Using the data from this test, calculate $V_{m(std)}$ the total volume of dry gas metered corrected to standard conditions (20^o C and 760 mm Hg), by using Equation 5-1 of Method 5. If necessary, adjust $V_{m(std)}$ for leakages as outlined in Section 6.3 of Method 5. See the field data sheet for the average dry gas meter temperature and average orifice pressure drop.

8.3 Volume of Water Vapor and Moisture content.
Using data obtained in this test and Equations 5-2 and 5-3 of Method 5, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas.

8.4 Total Cyanide in Sample.

Colorimetric Procedure. Use the following equation to calculate the

amount of CN^- in the sample:

$$m_t = \frac{10^{-3} \times V_t \times V_d C_c}{A_t \times A_d} \qquad \text{Eq. 1}$$

Titration Procedure. Use the following equation to calculate the amount of CN^- in the sample:

$$m_t = \frac{(T - B) \times V_t \times 250}{A_t \times Q_t} \qquad \text{Eq. 2}$$

8.5 Total Cyanide Concentration in Stack Gas.
Use the following equation to calculate total cyanide concentration in the stack gas:

$$C_s = \frac{K \times m_t}{V_{m(std)}} \qquad \text{Eq. 3}$$

Where:

K = 1.00 m^3/m^3 if $V_{m(std)}$ is expressed in metric units.

K = 35.31 ft^3/m^3 if $V_{m(std)}$ is expressed in English units.

8.5 Isokinetic Variation and Acceptable Results.
Same as Method 5, Sections 6.11 and 6.12, respectively. To calculate V_s the average stack gas velocity, use equation 2-9 of Method 2 and the data from this field test.

9. ALTERNATIVE TEST METHODS FOR TOTAL CYANIDE.

9.1 NIOSH Method 7904 (Reference 10.4).
Airborne cyanides (gas and aerosol) are collected on a cellulose ester membrane filter and in a KOH bubbler. Because the particulate cyanide collected on the filter can liberate HCN which is trapped in the bubbler, the method cannot distinguish between HCN formed in this manner and HCN originally present in the air. Cyanide concentration is determined with an ion-specific electrode.

Interferences are significant. Sulfide, iodide, bromide, cadmium, zinc,

silver, nickel, cuprous ion, and mercury are named as elements or compounds which affect the performance of the ion-specific electrode. Except for sulfide, the method does not propose remedies for minimizing or eliminating these interferences.

10. BIBLIOGRAPHY.

10.1 American Society for Testing and Materials. Annual Book of ASTM Standards. Part 31; Water, Atmospheric Analysis. Philadelphia, Pa. 1974. p. 40-42.

10.2 U.S. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., Method 9010. In "Test Methods for Evaluating Solid Waste-Physical/Chemical Methods" SW-846 (1982).

10.3 EPA-600/4-79-020. Method 335.2. In "Methods for Chemical Analysis of Water and Wastes" (Final report)/J.F. Kopp et al. Environmental Monitoring and Support Laboratory, Cincinnati, OH. March 1983.

10.4 NIOSH Manual of Analytical Methods, 3rd ed., Method 7904, Cyanides, Aerosol and gas. U.S. Department of Health and Human Services DHHS (NIOSH) Publ. No. 84-100. Feb, 1984.

10.5 Same as Method 5, Citations 2 to 5 and 7 of Section 7.

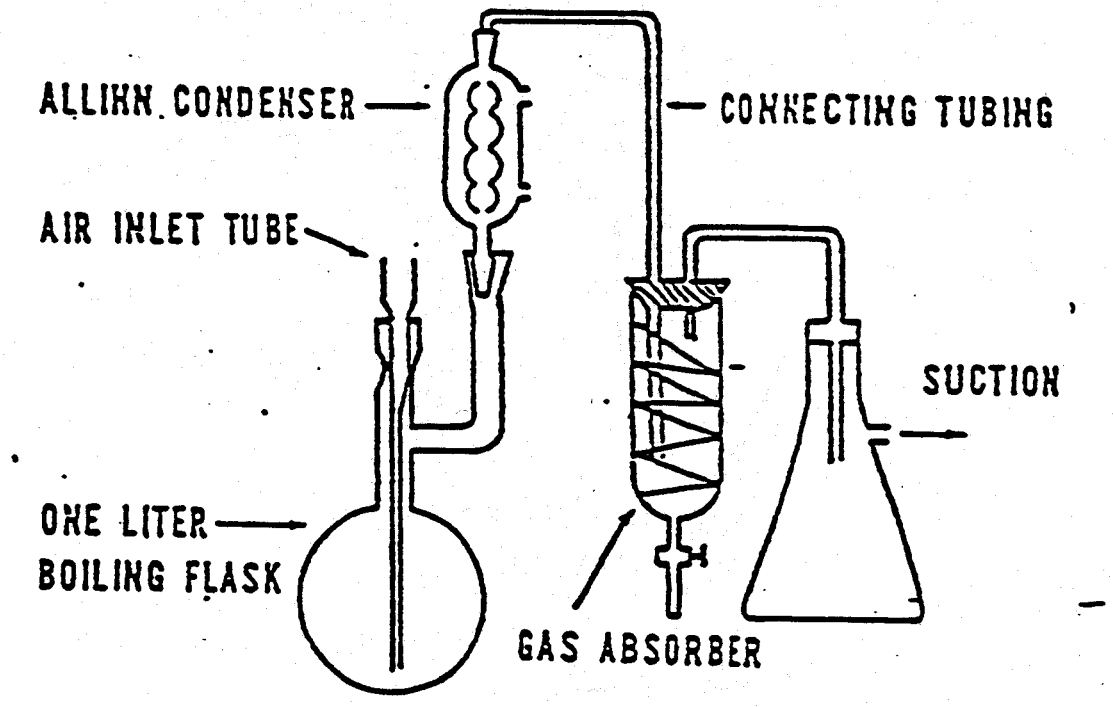

FIGURE 1

CYANIDE DISTILLATION APPARATUS

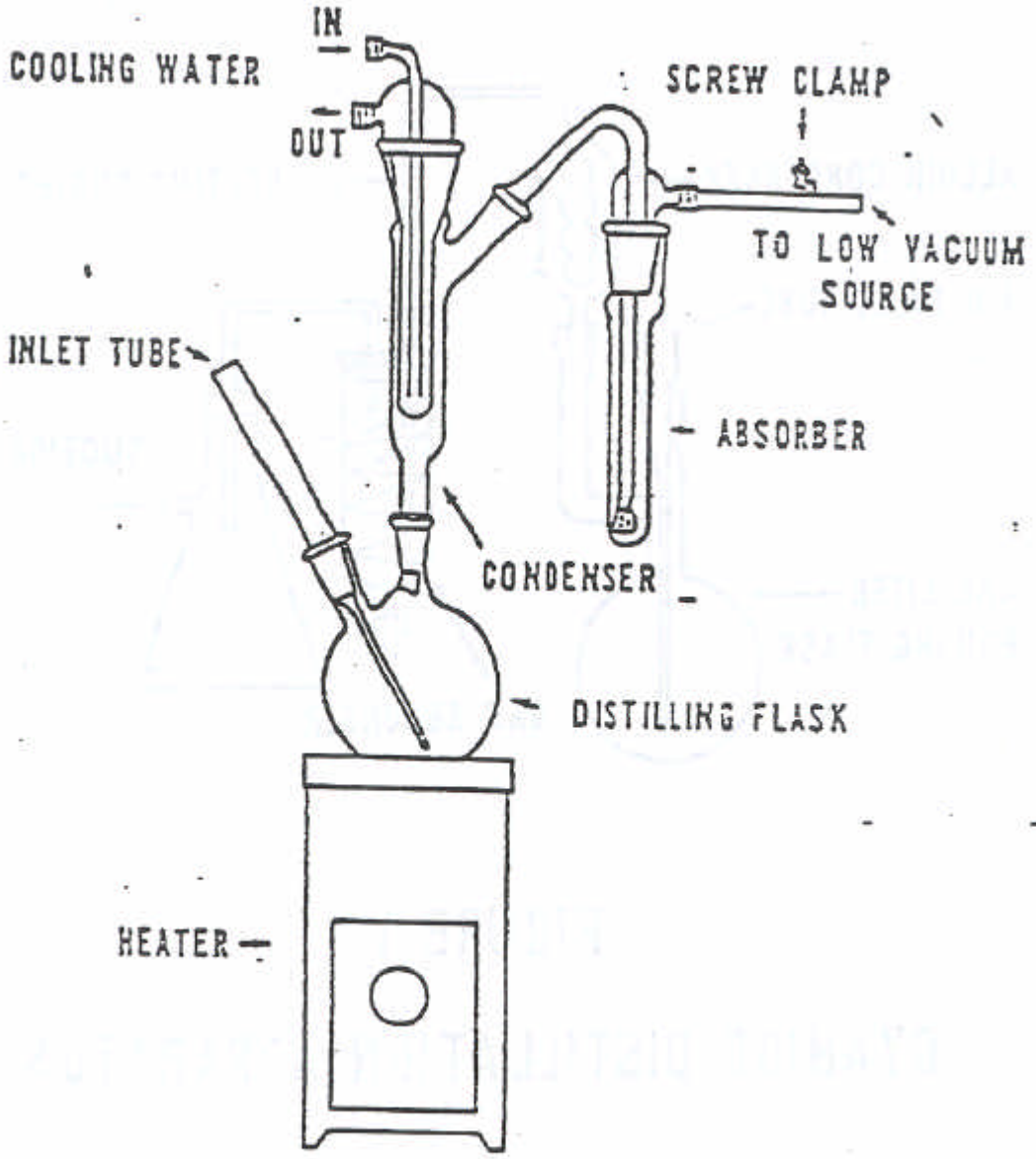

FIGURE 2

CYANIDE DISTILLATION APPARATUS

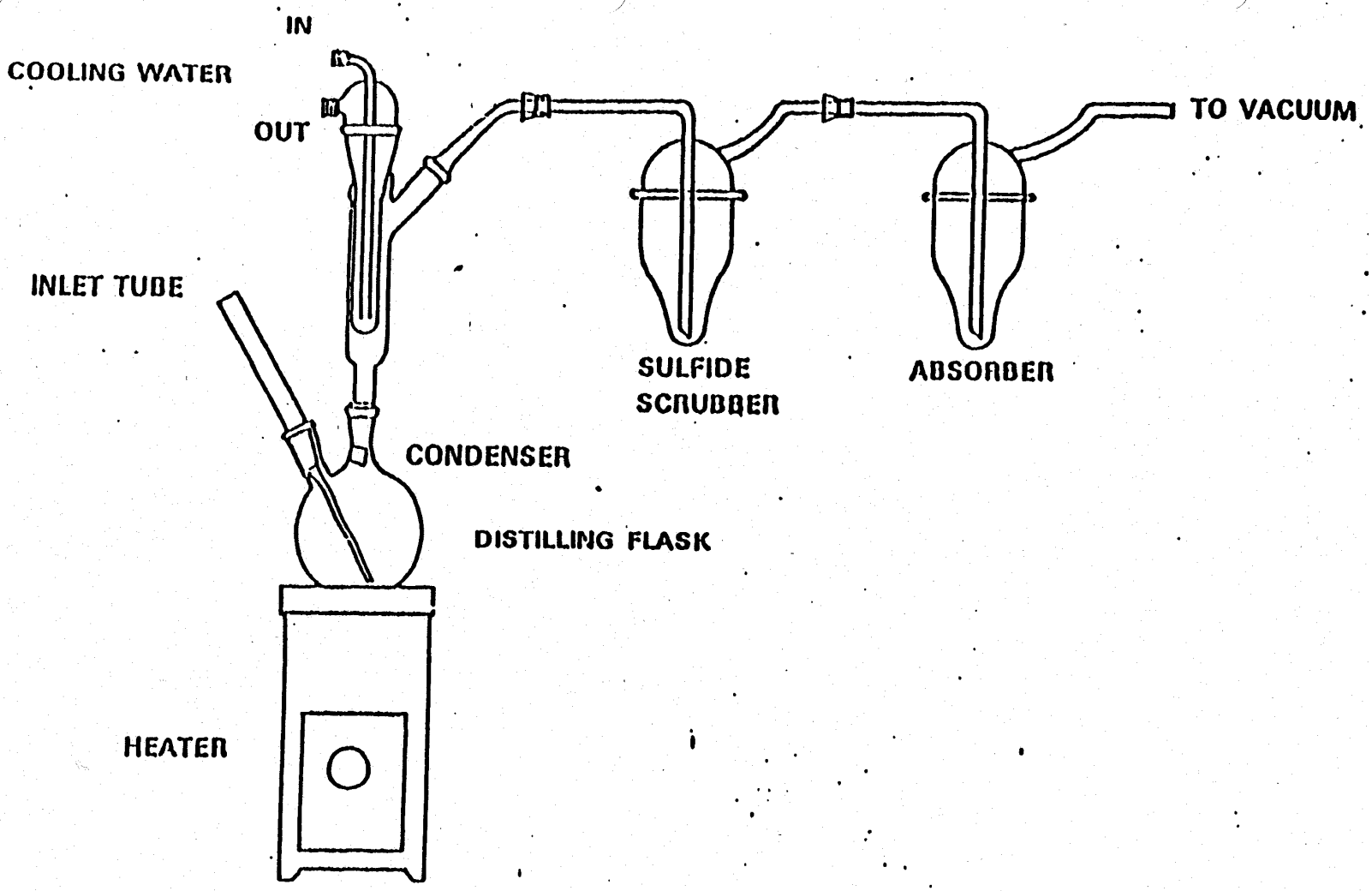

Figure 3.
Cyanide Distillation Apparatus