METHOD 9012B

TOTAL AND AMENABLE CYANIDE (AUTOMATED COLORIMETRIC, WITH OFF-LINE DISTILLATION)

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentration of inorganic cyanide (CAS Registry Number 57-12-5) in wastes or leachate. This method detects inorganic cyanides that are present as either soluble salts or complexes. It is used to determine values for both total cyanide and cyanide amenable to chlorination. The "reactive" cyanide content of a waste is not determined by this method. Refer to 40 CFR 261.23 for information on the characteristic of reactivity.

2.0 SUMMARY OF METHOD

2.1 The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by automated UV colorimetry.

2.2 In the automated colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction with Chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The concentration of NaOH must be the same in the standards, the scrubber solutions, and any dilution of the original scrubber solution to obtain colors of comparable intensity.

3.0 INTERFERENCES

3.1 Interferences are eliminated or reduced by using the distillation procedure. Chlorine and sulfide are interferences in this method.

3.2 Oxidizing agents such as chlorine decompose most cyanides. Chlorine interferences can be removed by adding an excess of sodium arsenite to the waste prior to preservation and storage of the sample to reduce the chlorine to chloride which does not interfere.

3.3 Sulfide interference can be removed by adding an excess of bismuth nitrate to the waste (to precipitate the sulfide) before distillation. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation should be treated by the addition of bismuth nitrate.

3.4 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds once formed will decompose under test conditions to generate HCN. The possibility of interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation. Nitrate and nitrite are interferences when present at levels higher than 10 mg/L and in conjunction with certain organic compounds.

3.5 Thiocyanate is reported to be an interference when present at very high levels. Levels of 10 mg/L were not found to interfere in Method 9010.

3.6 Fatty acids, detergents, surfactants, and other compounds may cause foaming during the distillation when they are present in large concentrations and will make the endpoint of the titration difficult to detect. They may be extracted at pH 6-7.

4.0 APPARATUS AND MATERIALS

4.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of one liter size with inlet tube and provision for condenser. The gas scrubber may be a 270-mL Fisher-Milligan scrubber (Fisher, Part No. 07-513 or equivalent). The reflux apparatus may be a Wheaton 377160 distillation unit or equivalent.

4.2 Automated continuous-flow analytical instrument with:

4.2.1 Sampler.

4.2.2 Manifold.

4.2.3 Proportioning pump.

4.2.4 Heating bath with distillation coil.

4.2.5 Distillation head.

4.2.6 Colorimeter equipped with a 15-mm flowcell and 570 nm filter.

4.2.7 Recorder.

4.3 Hot plate stirrer/heating mantle.

4.4 pH meter.

4.5 Amber light.

4.6 Vacuum source.

4.7 Refrigerator.

4.8 5 mL microburette.

4.9 7 Class A volumetric flasks -- 100 and 250 mL.

4.10 Erlenmeyer flask -- 500 mL.

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 Reagents for sample collection, preservation, and handling

5.3.1 Sodium arsenite (0.1N), $NaAsO_2$. Dissolve 3.2 g of $NaAsO_2$ in 250 mL water.

5.3.2 Ascorbic acid, $C_6H_8O_6$.

5.3.3 Sodium hydroxide solution (50%), NaOH. Commercially available.

5.3.4 Acetic acid (1.6M) CH_3COOH. Dilute one part of concentrated acetic acid with 9 parts of water.

5.3.5 2,2,4-Trimethylpentane, C_8H_{18}.

5.3.6 Hexane, C_6H_{14}.

5.3.7 Chloroform, $CHCl_3$.

5.4 Reagents for cyanides amenable to chlorination

5.4.1 Calcium hypochlorite solution (0.35M), $Ca(OCl)_2$. Combine 5 g of calcium hypochlorite and 100 mL of water. Shake before using.

5.4.2 Sodium hydroxide solution (1.25N), NaOH. Dissolve 50 g of NaOH in 1 liter of water.

5.4.3 Sodium arsenite (O.1N). See Sec. 5.3.1.

5.4.4 Potassium iodide starch paper.

5.5 Reagents for distillation

5.5.1 Sodium hydroxide (1.25N). See Sec. 5.4.2.

5.5.2 Bismuth nitrate (0.062M), $Bi(NO)_3 \cdot 5H_2O$. Dissolve 30 g of $Bi(NO)_3 \cdot 5H_2O$ in 100 mL of water. While stirring, add 250 mL of glacial acetic acid, CH_3COOH. Stir until dissolved and dilute to 1 liter with water.

5.5.3 Sulfamic acid (0.4N), H_2NSO_3H. Dissolve 40 g H_2NSO_3H in 1 liter of water.

5.5.4 Sulfuric acid (18N), H_2SO_4. Slowly and carefully add 500 mL of concentrated H_2SO_4 to 500 mL of water.

5.5.5 Magnesium chloride solution (2.5M), $MgCl_2 \cdot 6H_2O$. Dissolve 510 g of $MgCl_2 \cdot 6H_2O$ in 1 liter of water.

5.5.6 Lead acetate paper.

5.6 Reagents for automated colorimetric determination

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

5.6.2 Chloramine-T solution -- Dissolve 2.0 g of white, water soluble chloramine-T in 500 mL of reagent water and refrigerate until ready to use.

5.6.3 Sodium hydroxide, 1 N -- Dissolve 40 g of NaOH in reagent water, and dilute to 1 liter.

5.6.4 All working standards should contain 2 mL of 1 N NaOH (Sec. 5.6.3) per 100 mL.

5.6.5 Dilution water and receptacle wash water (NaOH, 0.25 N) -- Dissolve 10.0 g of NaOH in 500 mL of reagent water. Dilute to 1 liter.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Samples should be collected in plastic or glass containers. All containers must be thoroughly cleaned and rinsed.

6.2 Oxidizing agents such as chlorine decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with potassium iodide-starch test paper. A blue color indicates the need for treatment. Add 0.1N sodium arsenite solution a few mL at a time until a drop of sample produces no color on the indicator paper. Add an additional 5 mL of sodium arsenite solution for each liter of sample. Ascorbic acid can be used as an alternative although it is not as effective as arsenite. Add a few crystals of ascorbic acid 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.

6.3 Aqueous samples must be preserved by adding 50% sodium hydroxide until the pH is greater than or equal to 12 at the time of collection.

6.4 Samples should be chilled to 4 EC.

6.5 When properly preserved, cyanide samples can be stored for up to 14 days prior to sample preparation steps.

6.6 Solid and oily wastes may be extracted prior to analysis by Method 9013 (Cyanide Extraction Procedure for Solids and Oils). It uses a dilute NaOH solution (pH = 12) as the extractant. This yields extractable cyanide.

6.7 If fatty acids, detergents, and surfactants are a problem, they may be extracted using the following procedure. Acidify the sample with acetic acid (1.6M) to pH 6.0 to 7.0.

CAUTION: This procedure can produce lethal HCN gas.

Extract with isooctane, hexane, or chloroform (preference in order named) with solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the

compounds below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with 50% NaOH solution.

7.0 PROCEDURE

7.1 Pretreatment for cyanides amenable to chlorination

7.1.1 This test must be performed under amber light. $K_3[Fe\text{-}(CN)_6]$ may decompose under UV light and hence will test positive for cyanide amenable to chlorination if exposed to fluorescent lighting or sunlight. Two identical sample aliquots are required to determine cyanides amenable to chlorination.

7.1.2 To one 500 mL sample or to a sample diluted to 500 mL, add calcium hypochlorite solution dropwise while agitating and maintaining the pH between 11 and 12 with 1.25N sodium hydroxide until an excess of chlorine is present as indicated by KI-starch paper turning blue. The sample will be subjected to alkaline chlorination by this step.

CAUTION: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is necessary that this reaction be performed in a hood.

7.1.3 Test for excess chlorine with KI-starch paper and maintain this excess for one hour with continuous agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional calcium hypochlorite solution.

7.1.4 After one hour, add 1 mL portions of 0.1N sodium arsenite until KI-starch paper shows no residual chlorine. Add 5 mL of excess sodium arsenite to ensure the presence of excess reducing agent.

7.1.5 Test for total cyanide as described below in both the chlorinated and the unchlorinated samples. The difference of total cyanide in the chlorinated and unchlorinated samples is the cyanide amenable to chlorination.

7.1.6 If samples are known or suspected to contain sulfide, add 50 mL of 0.062M bismuth nitrate solution through the air inlet tube. Mix for three minutes. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper.

7.2 Distillation procedure

7.2.1 Place 500 mL of sample, or sample diluted to 500 mL in the one liter boiling flask. Pipet 50 mL of 1.25N sodium hydroxide into the gas scrubber. If the apparatus in Figure 1 is used, add water until the spiral is covered. Connect the boiling flask, condenser, gas scrubber and vacuum trap.

7.2.2 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 air inlet tube.

7.2.3 If samples are known or suspected to contain nitrate or nitrite, or if bismuth nitrate was added to the sample, add 50 mL of 0.4N sulfamic acid solution through the air inlet tube. Mix for three minutes.

NOTE: Excessive use of sulfamic acid could create method bias.

7.2.4 Slowly add 50 mL of 18N sulfuric acid through the air inlet tube. Rinse the tube with water and allow the airflow to mix the flask contents for three minutes. Add 20 mL of 2.5M magnesium chloride through the air inlet and wash the inlet tube with a stream of water.

7.2.5 Heat the solution to boiling. Reflux for one hour. Turn off heat and continue the airflow for at least 15 min. After cooling the boiling flask, and closing the vacuum source, disconnect the gas scrubber.

7.2.6 Transfer the solution from the scrubber into a 250-mL volumetric flask. Rinse the scrubber into the volumetric flask. Dilute to volume with water.

7.3 Automated colorimetric determination

7.3.1 Set up the manifold in a hood or a well-ventilated area as shown in Figure 3.

7.3.2 Allow colorimeter and recorder to warm up for 30 min. Run a baseline with all reagents, feeding reagent water through the sample line.

7.3.3 Place appropriate standards in the sampler in order of increasing concentration. Complete loading of the sampler tray with unknown samples.

7.3.4 When the baseline becomes steady, begin the analysis.

7.4 Standard curve for samples without sulfide

7.4.1 Prepare a series of standards by pipetting suitable volumes of working standard potassium cyanide solution into 250-mL volumetric flasks. To each flask, add 50 mL of 1.25N sodium hydroxide and dilute to 250 mL with water. Prepare using the following table. The sodium hydroxide concentration will be 0.25N.

mL of Working Standard Solution (1 mL = 10 µg CN^-)	Concentration (µg CN^-/L)
0.0	Blank
1.0	40
2.0	80
5.0	200
10.0	400
15.0	600
20.0	800

7.4.2 After the standard solutions have been prepared according to the table above, pipet 50 mL of each standard solution into a 100-mL volumetric flask and proceed

to Secs. 7.3.2 and 7.3.3 to obtain absorbance values for the standard curve. The final concentrations for the standard curve will be one half of the amounts in the above table (final concentrations ranging from 20 to 400 µg/L).

7.4.3 It is recommended that at least two standards (a high and a 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 ± 10% of the undistilled standards, the analyst should find the cause of the apparent error before proceeding.

7.4.4 Prepare a standard curve ranging from 20 to 400 µg/L by plotting absorbance of standard versus the cyanide concentration

7.5 Standard curve for samples with sulfide

7.5.1 It is imperative that all standards be distilled in the same manner as the samples using the method of standard additions (for example, bismuth nitrate must also be added to the standards). Standards distilled by this method will give a linear curve, at low concentrations, but as the concentration increases, the recovery decreases. It is recommended that at least five standards be distilled.

7.5.2 Prepare a series of standards similar in concentration to those mentioned in Sec. 7.4.1 and analyze as in Sec. 7.3. Prepare a standard curve by plotting absorbance of standard versus the cyanide concentration.

7.6 Calculation -- Prepare a standard curve by plotting peak heights of standards against their concentration values. Compute concentrations of samples by comparing sample peak heights with the standard curve.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Verify the calibration curve with an independent calibration check standard. If the standards are not within 15% of the expected value, a new recalibration curve is required. Verify the calibration curve with every sample batch by analyzing a mid-range standard.

8.3 Run one matrix spike sample for every 10 samples to check the efficiency of sample distillation. A matrix spike should be prepared by adding cyanide from the working standard or intermediate standard to 500 mL of sample to ensure a concentration of approximately 40 µg/L. Both the matrix duplicate and matrix spike duplicate are brought through the entire sample preparation and analytical process.

8.4 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences such as samples which contain sulfides.

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are not available at this time.

10.0 REFERENCES

1. Annual Book of ASTM Standards, Part 31, "Water," Standard D2036-75, Method B, p. 505 (1976).

2. Goulden, P.D., B.K. Afghan, and P. Brooksbank, Determination of Nanogram Quantities of Simple and Complex Cyanides in Water, Anal. Chem., 44(11), pp. 1845-49 (1972).

3. Standard Methods for the Examination of Water and Wastewater, 14th ed., pp. 376 and 370, Method 413F and D (1975).

4. Technicon AutoAnalyzer II Methodology, Industrial Method No. 315-74 WCUV Digestion and Distillation, Technicon Industrial Systems, Tarrytown, New York, 10591 (1974).

FIGURE 1
APPARATUS FOR CYANIDE DISTILLATION

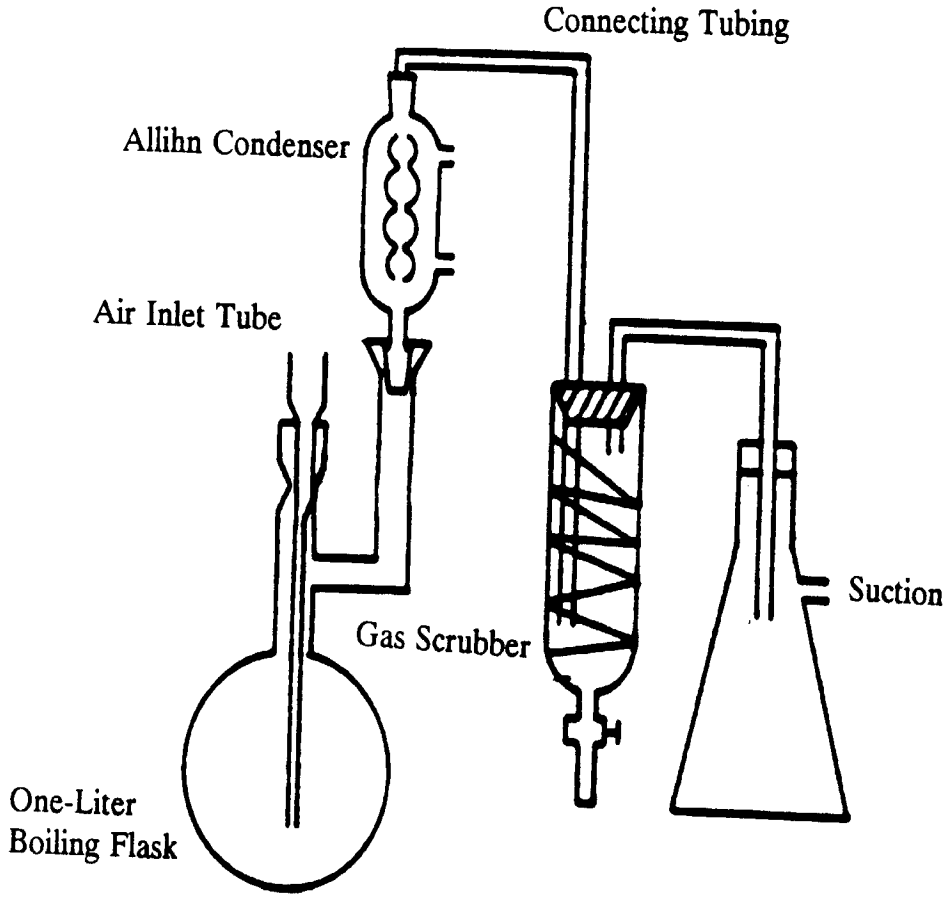


FIGURE 2
CYANIDE DISTILLATION APPARATUS

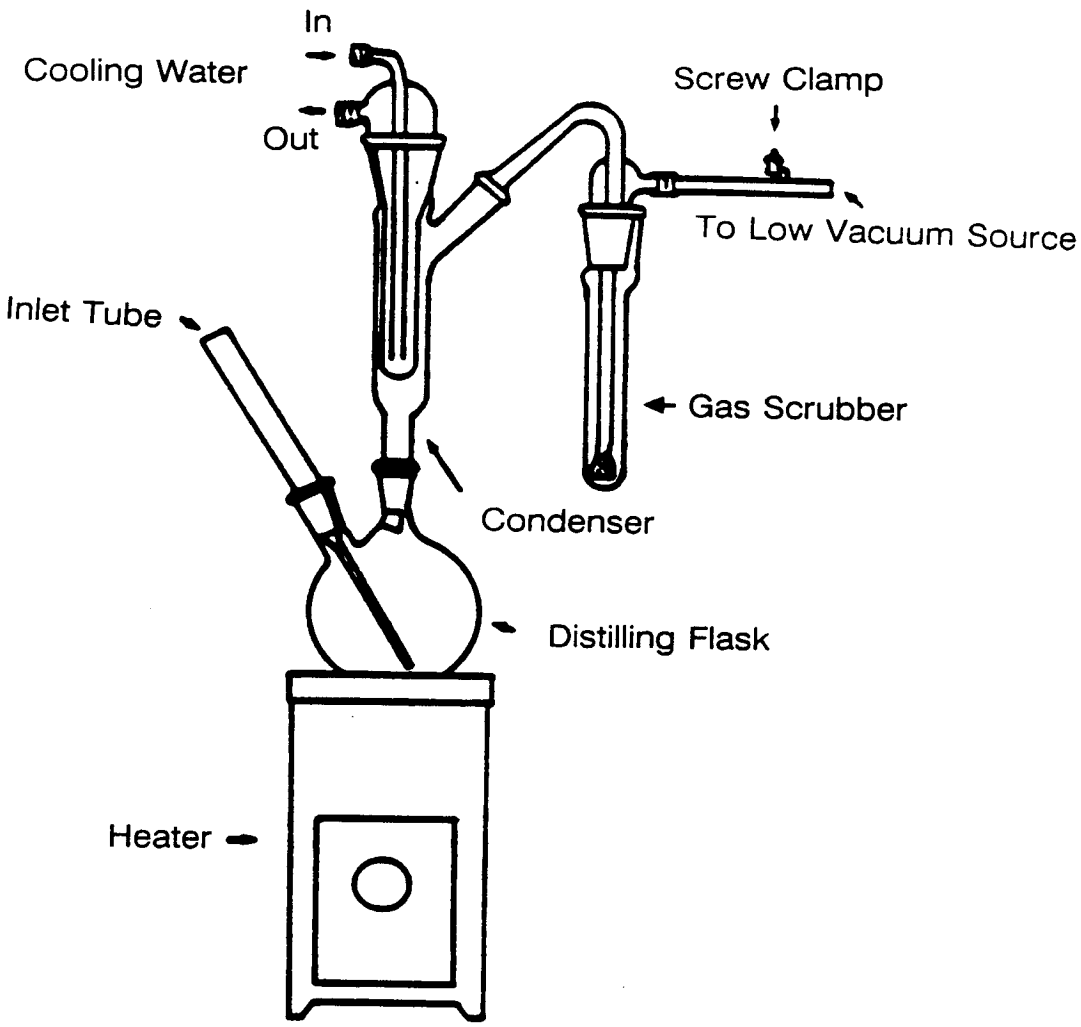
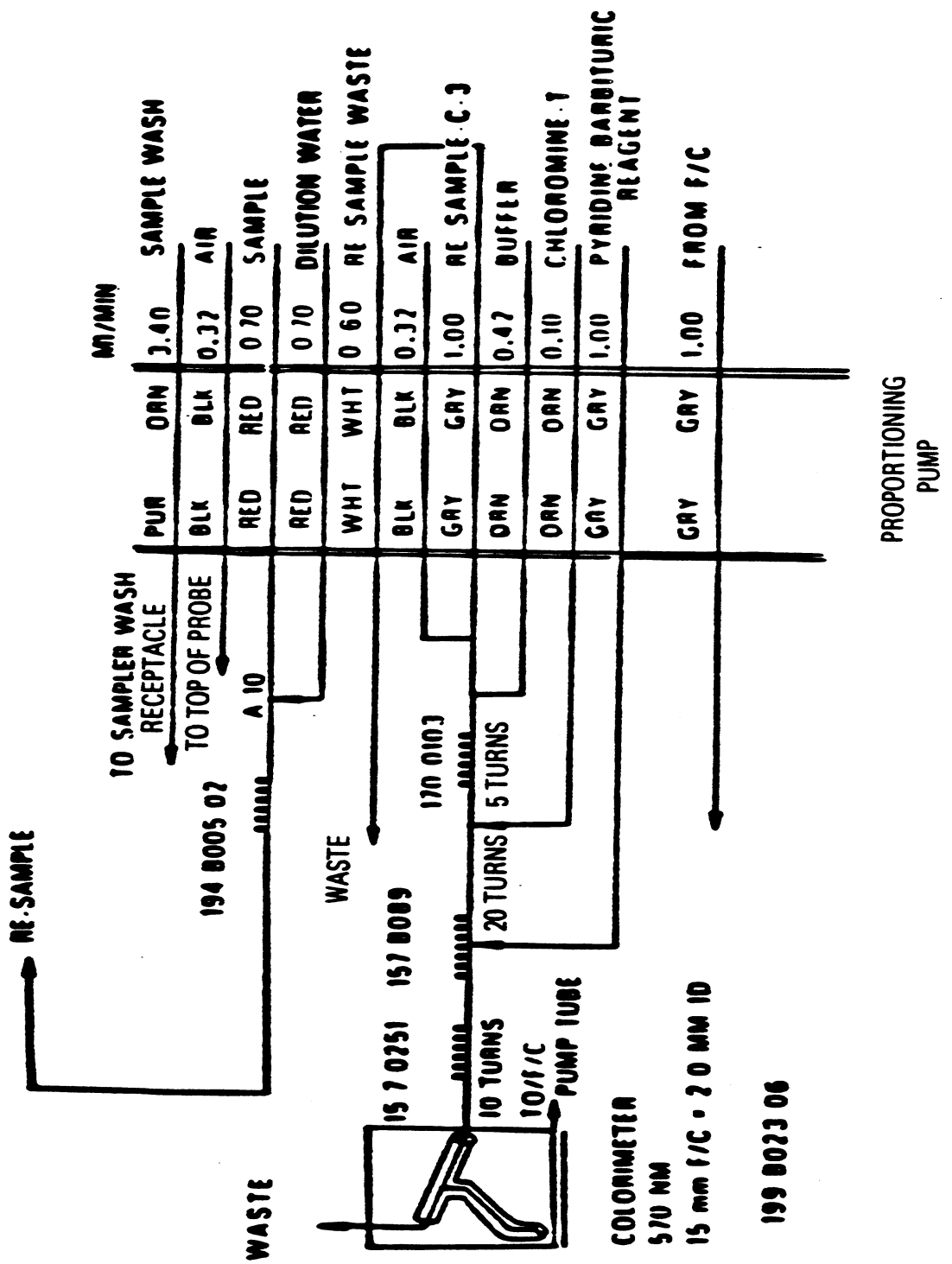
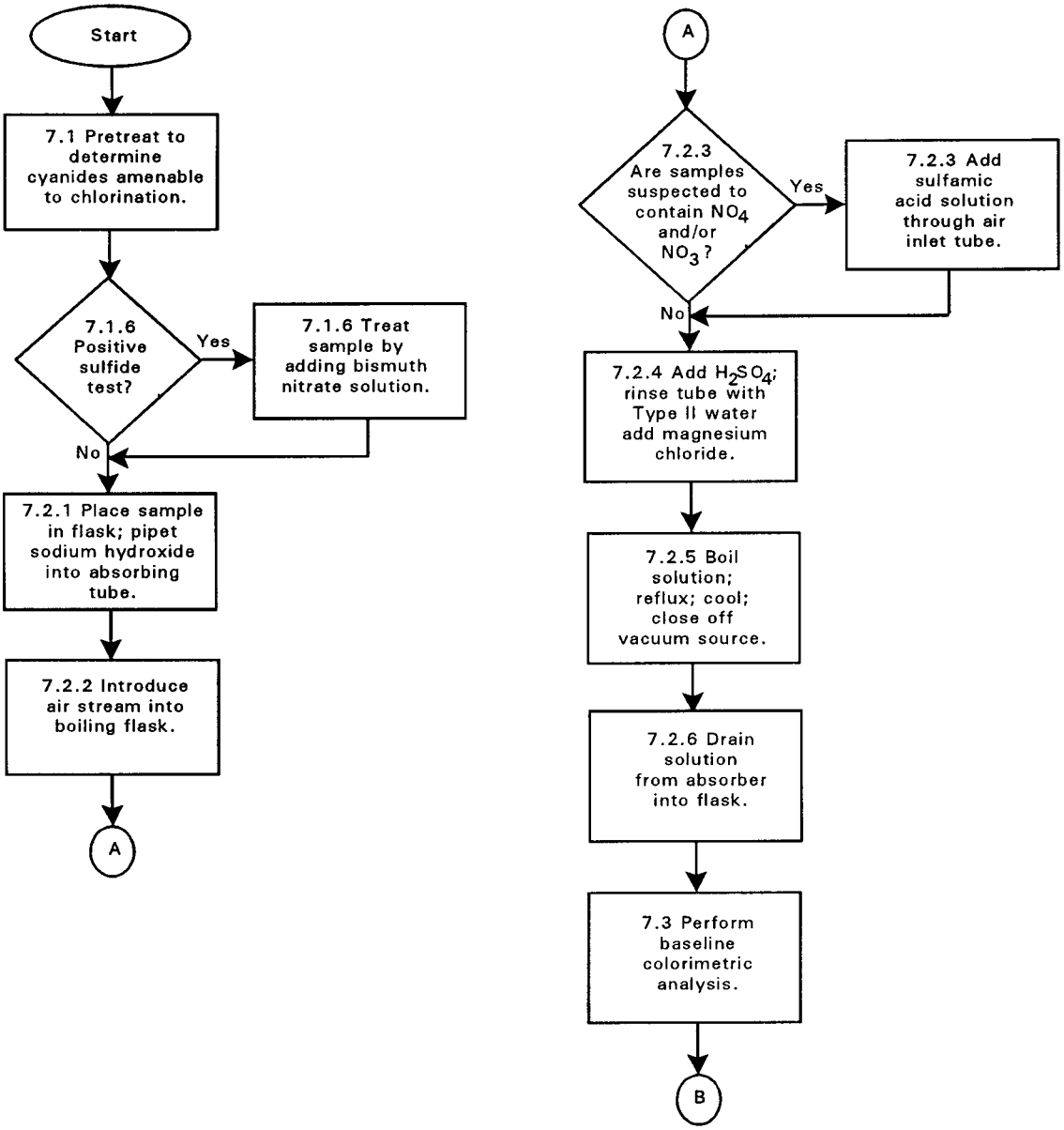
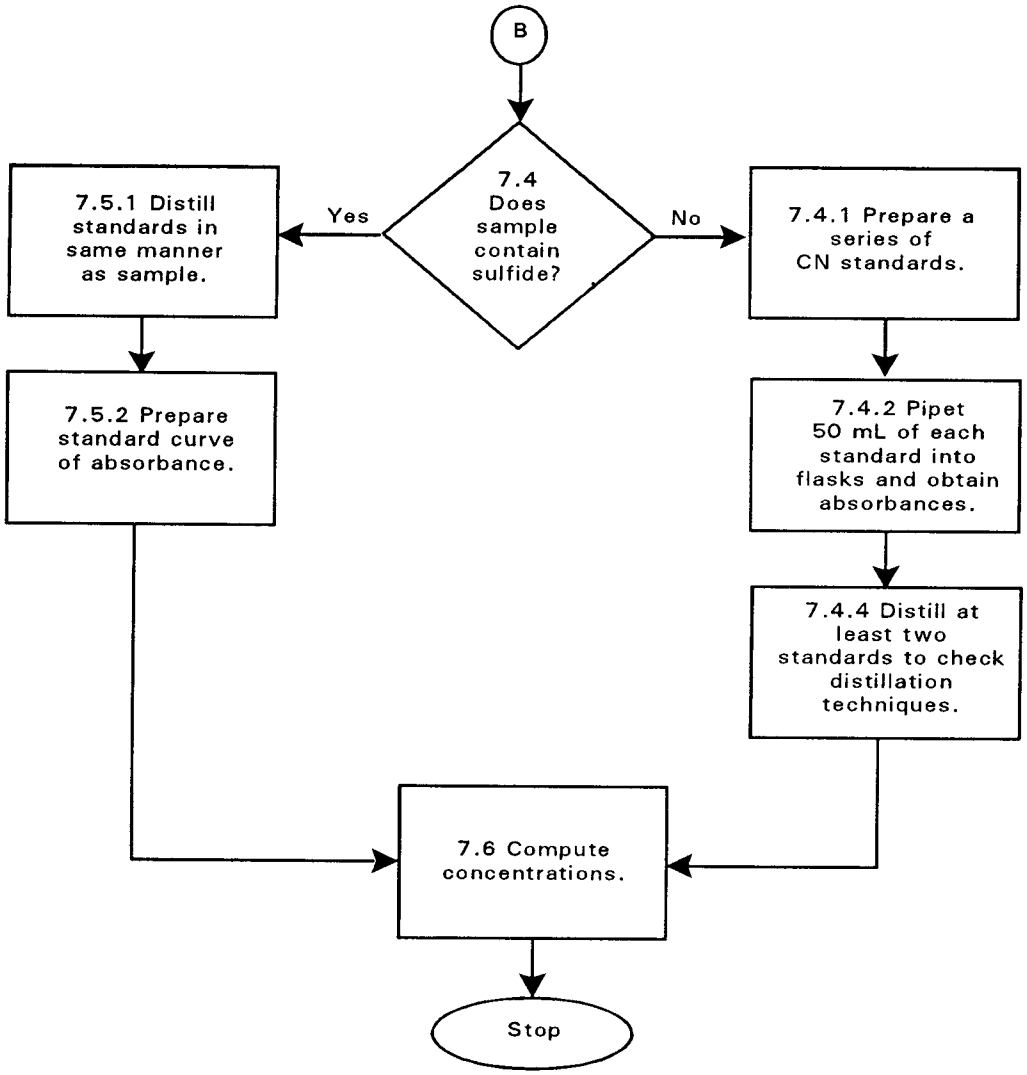


FIGURE 3
CYANIDE MANIFOLD AA11



TOTAL AND AMENABLE CYANIDE (AUTOMATED COLORIMETRIC WITH OFF-LINE DISTILLATION)

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7.4 Does sample contain sulfide?
Yes
No
7.5.1 Distill standards in same manner as sample.
7.5.2 Prepare standard curve of absorbance.
7.4.1 Prepare a series of CN standards.
7.4.2 Pipet 50 mL of each standard into flasks and obtain absorbances.
7.4.4 Distill at least two standards to check distillation techniques.
7.6 Compute concentrations.
Stop