TOTAL AND AMENABLE CYANIDE (COLORIMETRIC, AUTOMATED UV)

1.0 SCOPE AND APPLICATION

1.1 Method 9012 is used to determine the concentration of inorganic cyanide in an aqueous waste or leachate. The method detects inorganic cyanides that are present as either simple soluble salts or complex radicals. It is used to determine values for both total cyanide and cyanide amenable to chlorination. Method 9012 is not intended to determine if a waste is hazardous by the characteristic of reactivity.

2.0 SUMMARY OF METHOD

2.1 The cyanide, as hydrocyanic acid (HCN), is released by refluxing the sample with strong acid and distillation of the HCN into an absorber-scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by automated UV colorimetry.

2.2 In the 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 procedures described in Paragraphs 7.2.3, 7.2.4, and 7.2.5.

3.2 Sulfides adversely affect the colorimetric procedures. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation should be treated by addition of bismuth nitrate prior to distillation as described in Paragraph 7.2.3.

3.3 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 will decompose under test conditions to generate HCN. The possible interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

4.0 APPARATUS AND MATERIALS

4.1 Reflux distillation apparatus: Such as shown in Figure 1 or 2. The boiling flask should be of 1-liter size with inlet tube and provision for condenser. The gas absorber is a Fisher-Milligan scrubber (Fisher Catalog #07-513) or equivalent.

4.2 Potassium iodide-starch test paper.

4.3 Automated continuous-flow analytical instrument with:

4.3.1 **Sampler.**
4.3.2 **Manifold with UV digestor.**
4.3.3 **Proportioning pump.**
4.3.4 **Heating bath with distillation coil.**
4.3.5 **Distillation head.**
4.3.6 **Colorimeter equipped with a 15-mm flowcell and 570 nm filter.**
4.3.7 **Recorder.**

5.0 REAGENTS

5.1 ASTM Type II water (ASTM D1193): Water should be monitored for impurities.

5.2 Sodium hydroxide solution, 1.25 N: Dissolve 50 g of NaOH in Type II water and dilute to 1 liter with Type II water.

5.3 Bismuth nitrate solution: Dissolve 30.0 g of $Bi(NO_3)_3$ in 100 mL of Type II water. While stirring, add 250 mL of glacial acetic acid. Stir until dissolved. Dilute to 1 liter with Type II water.

5.4 Sulfuric acid, 1:1: Slowly add 500 mL of concentrated H_2SO_4 to 500 mL of Type II water.
CAUTION: this is an exothermic reaction.

5.5 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 liter of Type II water.

5.6 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of Type II water. Standardize with 0.0192 N $AgNO_3$. Dilute to appropriate concentration so that 1 mL = 1 mg CN.

5.7 Intermediate standard cyanide solution: Dilute 100.0 mL of stock (1 mL = 1 mg CN) to 1,000 mL with Type II water (1 mL = 100 ug CN).

5.8 Working standard cyanide solution: Prepare fresh daily by diluting 100.0 mL of intermediate cyanide solution to 1,000 mL with Type II water (1 mL = 10.0 ug CN). Store in a glass-stoppered bottle.

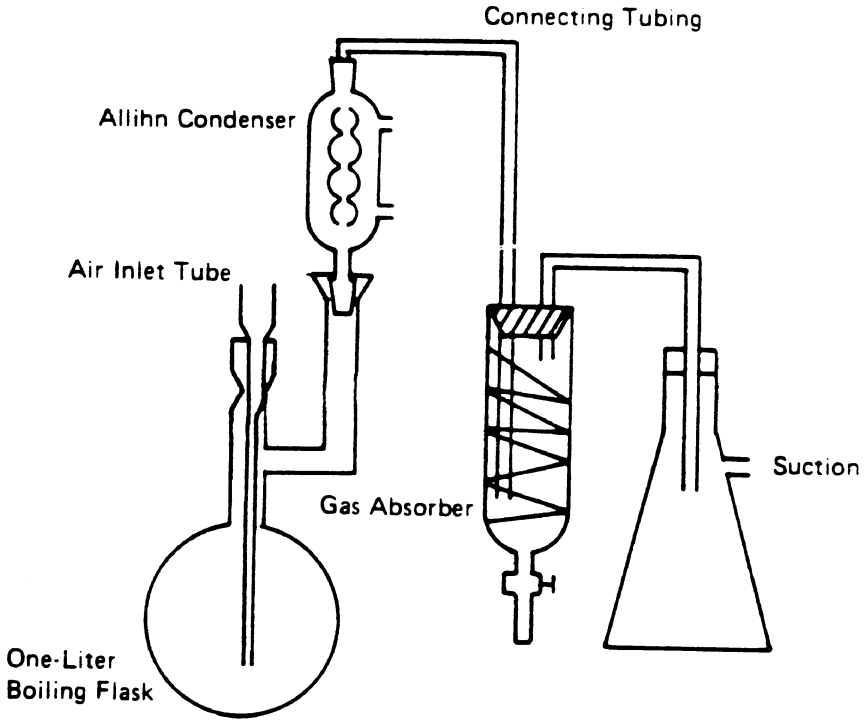


Figure 1. Apparatus for cyanide distillation.

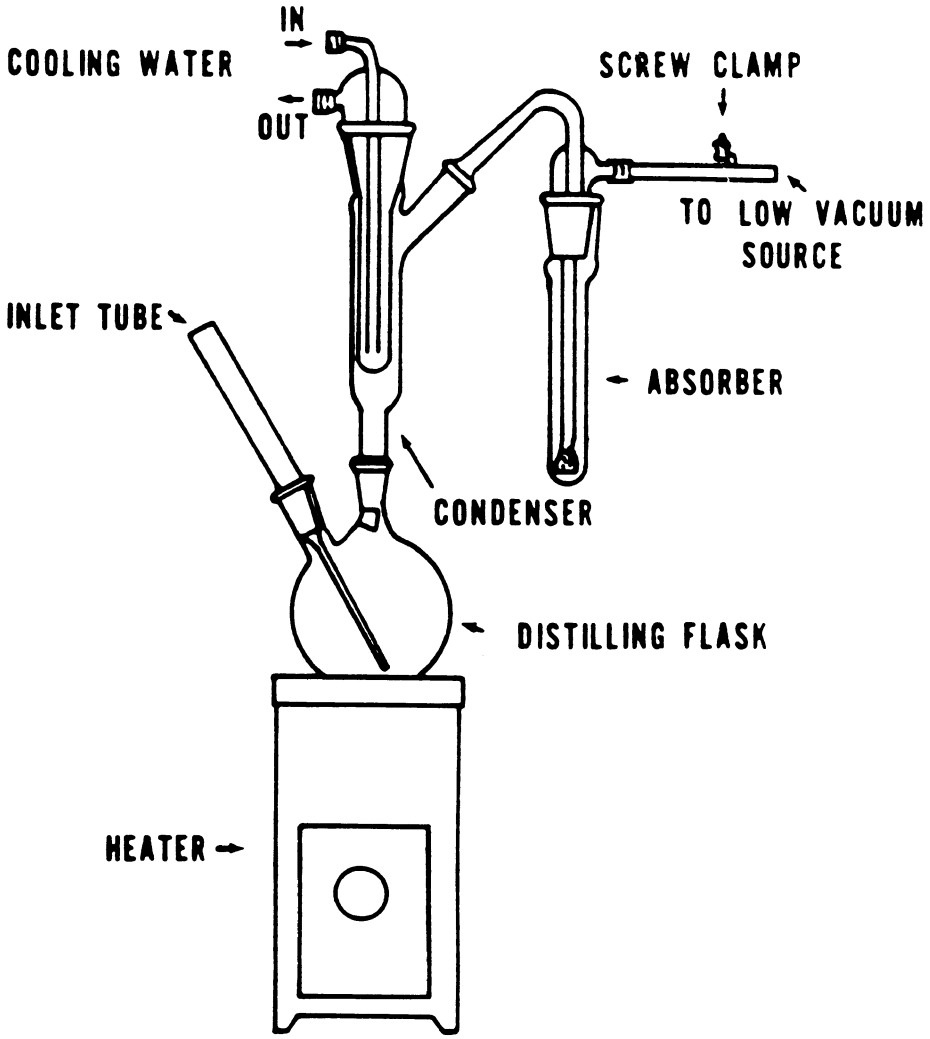


Figure 2. Cyanide distillation apparatus.

5.9 Magnesium chloride solution: Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1,000-mL flask, dissolve, and dilute to 1 liter with Type II water.

5.10 Sulfamic acid solution: Dissolve 40 g of sulfamic acid in Type II water. Dilute to 1 liter.

5.11 Calcium hypochlorite solution: Dissolve 5 g of calcium hypochlorite [$Ca(OCl)_2$] in 100 mL of Type II water.

5.12 Reagents for automated colorimetric determination:

5.12.1 **Pyridine-barbituric acid reagent:** Place 15 g of barbituric acid in a 250-mL volumetric flask, add just enough Type II 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 Type II water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

5.12.2 **Chloramine-T solution:** Dissolve 2.0 g of white, water soluble chloramine-T in 500 mL of Type II water and refrigerate until ready to use.

5.12.3 **Sodium hydroxide**, 1 N: Dissolve 40 g of NaOH in Type II water, and dilute to 1 liter.

5.12.4 All **working standards** should contain 2 mL of 1 N NaOH (Paragraph 5.12.3) per 100 mL.

5.12.5 **Dilution water and receptacle wash water** (NaOH, 0.25 N): Dissolve 10.0 g NaOH in 500 mL of Type II water. Dilute to 1 liter.

5.13 Ascorbic acid: Crystals.

5.14 Phosphate buffer, pH 5.2: Dissolve 13.6 g of potassium dihydrogen phosphate and 0.28 g of disodium phosphate in 900 mL of Type II water 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 Samples should be collected in plastic or glass bottles of 1-liter size or larger. All bottles must be thoroughly cleaned and thoroughly rinsed to remove soluble materials from containers.

6.3 Oxidizing agents such as chlorine decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with acidified potassium iodide (KI)-starch test paper at the time the sample is collected; 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. Then add an additional 0.6 g of ascorbic acid for each liter of water.

6.4 Samples must be preserved by addition of 10 N sodium hydroxide until sample pH is greater than or equal to 12 at the time of collection.

6.5 Samples should be refrigerated at 4°C, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Pretreatment for cyanides amenable to chlorination:

7.1.1 Two sample aliquots are required to determine cyanides amenable to chlorination. To one 500-mL aliquot, or to a volume diluted to 500 mL, add calcium hypochlorite solution (Paragraph 5.11) dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide (Paragraph 5.2).

CAUTION: The initial reaction product of alkaline chlorination is the very toxic gas **cyanogen chloride**; therefore, it is recommended that this reaction be performed in a hood. For convenience, the sample may be agitated in a 1-liter beaker by means of a magnetic stirring device.

7.1.2 Test for residual chlorine with KI-starch paper (Paragraph 4.4) and maintain this excess for 1 hr, continuing agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional hypochlorite solution.

7.1.3 After 1 hr, add 0.5 g portions of ascorbic acid until KI-starch paper shows no residual chlorine. Add an additional 0.5 g of ascorbic acid to ensure the presence of excess reducing agent.

7.1.4 Test for total cyanide in both the chlorinated and unchlorinated aliquots. (The difference of total cyanide in the chlorinated and unchlorinated aliquots is the cyanide amenable to chlorination.)

7.2 Distillation Procedure:

7.2.1 Place 500 mL of sample, or an aliquot diluted to 500 mL, in the 1-liter boiling flask. Pipet 50 mL of sodium hydroxide (Paragraph 5.2) into the absorbing tube. If the apparatus in Figure 1 is used, add Type II water until the spiral is covered. Connect the boiling flask, condenser, absorber, and trap in the train (Figure 1 or 2).

7.2.2 By adjusting the vacuum source, start a slow stream of air entering the boiling flask so that approximately two bubbles of air per second enter the flask through the air inlet tube.

7.2.3 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. If positive, treat the sample by adding 50 mL of bismuth nitrate solution (Paragraph 5.3) through the air inlet tube after the air rate is set. Mix for 3 min prior to addition of H_2SO_4.

7.2.4 If samples are suspected to contain NO_3 and/or NO_2, add 50 mL of sulfamic acid solution (Paragraph 5.10) after the air rate is set through the air inlet tube. Mix for 3 min prior to addition of H_2SO_4.

7.2.5 Slowly add 50 mL 1:1 H_2SO_4 (Paragraph 5.4) through the air inlet tube. Rinse the tube with Type II water and allow the airflow to mix the flask contents for 3 min. Pour 20 mL of magnesium chloride (Paragraph 5.9) into the air inlet and wash down with a stream of water.

7.2.6 Heat the solution to boiling. Reflux for 1 hr. Turn off heat and continue the airflow for at least 15 min. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

7.2.7 Drain the solution from the absorber into a 250-mL volumetric flask. Wash the absorber with Type II water and add the washings to the flask. Dilute to the mark with Type II 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 Type II water through the sample line.

7.3.3 Place appropriate standards in the sampler in order of decreasing 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 standard solution (Paragraph 5.8) into 250-mL volumetric flasks. To each standard add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with Type II water. Prepare as follows:

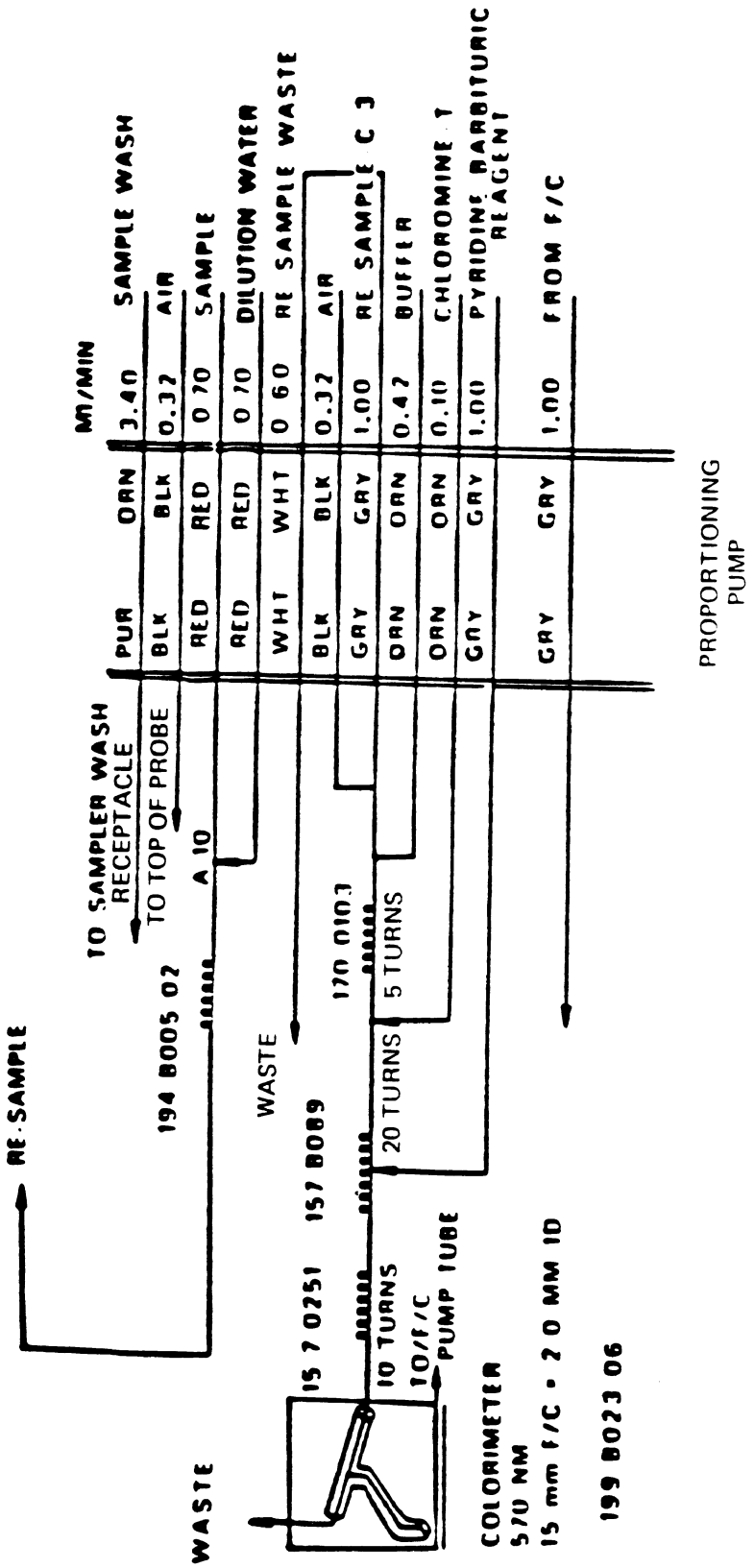


Figure 3. Cyanide manifold AA11.

mL of Working Standard Solution (1 mL = 10 ug CN)	Concentration (ug CN/250 mL)
0	BLANK
1.0	10
2.0	20
5.0	50
10.0	100
15.0	150
20.0	200

7.4.2 It is not imperative that all standards be distilled in the same manner as the samples. It is recommended that at least two standards (a high and a low) be distilled and compared with 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 analyst should find the cause of the apparent error before proceeding.

7.4.3 Prepare a standard curve by plotting absorbances of standards vs. cyanide concentrations.

7.4.4 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (Paragraph 5.7) or the working standard (Paragraph 5.8) to 500 mL of sample to ensure a level of 20 ug/L. Proceed with the analysis as in Paragraph 7.2.1.

7.5 Standard curve for samples with sulfide:

7.5.1 All standards must be distilled in the same manner as the samples. A minimum of 3 standards shall be distilled.

7.5.2 Prepare a standard curve by plotting absorbances of standards vs. 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 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring.

8.3 Verify calibration with an independently prepared check standard every 15 samples.

8.4 Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process.

8.5 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences.

9.0 METHOD PERFORMANCE

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

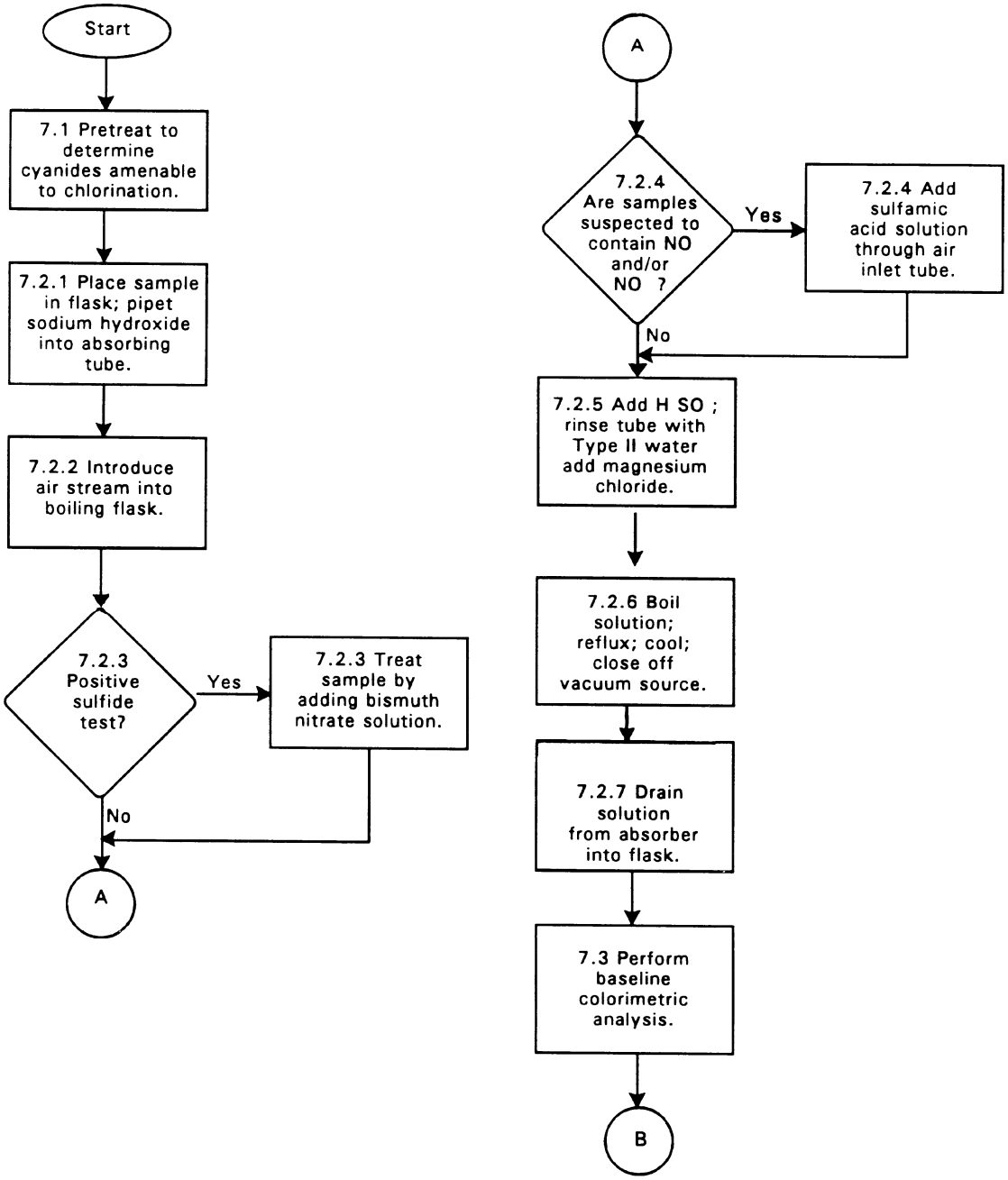
10.0 REFERENCES

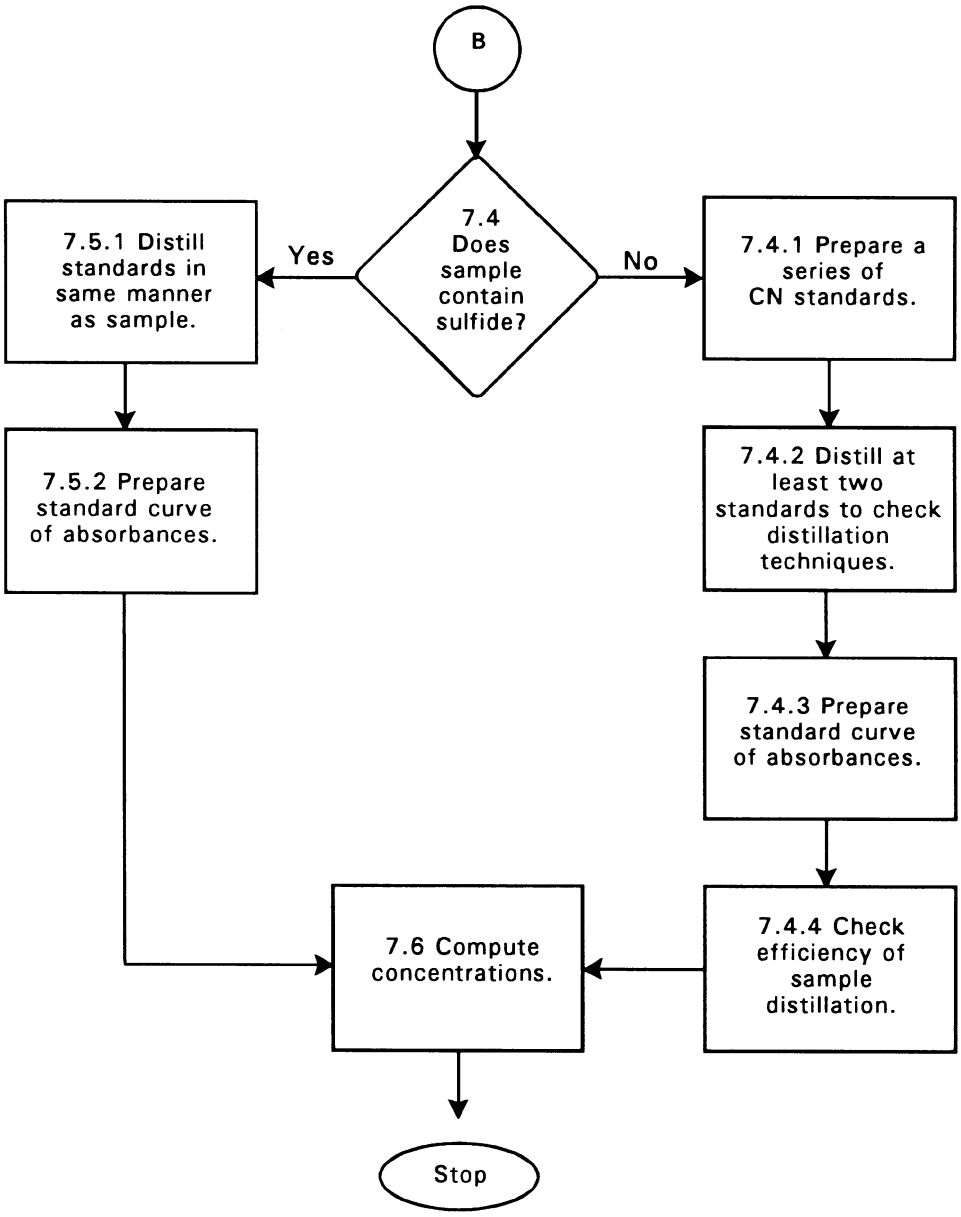
1. Annual Book of ASTM Standards, Part 31, "Water," Standard D2036-75, Method B, p. 505 (1976).

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).


Start
7.1 Pretreat to determine cyanides amenable to chlorination.
7.2.1 Place sample in flask; pipet sodium hydroxide into absorbing tube.
7.2.2 Introduce air stream into boiling flask.
7.2.3 Positive sulfide test?
Yes
7.2.3 Treat sample by adding bismuth nitrate solution.
No
A
A
7.2.4 Are samples suspected to contain NO and/or NO ?
Yes
7.2.4 Add sulfamic acid solution through air inlet tube.
No
7.2.5 Add H SO ; rinse tube with Type II water add magnesium chloride.
7.2.6 Boil solution; reflux; cool; close off vacuum source.
7.2.7 Drain solution from absorber into flask.
7.3 Perform baseline colorimetric analysis.
B


B
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 absorbances.
7.4.1 Prepare a series of CN standards.
7.4.2 Distill at least two standards to check distillation techniques.
7.4.3 Prepare standard curve of absorbances.
7.4.4 Check efficiency of sample distillation.
7.6 Compute concentrations.
Stop