METHOD 9010B

TOTAL AND AMENABLE CYANIDE: DISTILLATION

1.0 SCOPE AND APPLICATION

1.1 Method 9010 is reflux-distillation procedure used to extract soluble cyanide salts and many insoluble cyanide complexes from wastes and leachates. It is based on the decomposition of nearly all cyanides by a reflux distillation procedure using a strong acid and a magnesium catalyst. Cyanide, in the form of hydrocyanic acid (HCN) is purged from the sample and captured into an alkaline scrubber solution. The concentration of cyanide in the scrubber solution is then determined by Method 9014 or Method 9213. Method 9010 may be used as a reflux-distillation procedure for both total cyanide and cyanide amenable to chlorination. The "reactive" cyanide content of a waste, that is, the cyanide content that could generate toxic fumes when exposed to mild acidic conditions, is not determined by this method. Refer to Chapter Seven of SW-846 for the additional information on reactive cyanide.

1.2 This method was designed to address the problem of "trace" analyses (<1000 ppm). The method may also be used for "minor" (1000 ppm - 10,000 ppm) and "major" (>10,000 ppm) analyses by adapting the appropriate sample dilution. However, the amount of sodium hydroxide in the standards and the sample analyzed must be the same.

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 concentration in the absorbing solution is then determined colorimetrically or titrametrically by Method 9014 or by ion-selective electrode by Method 9213.

3.0 INTERFERENCES

3.1 Interferences are eliminated or reduced by using the distillation procedure. Chlorine and sulfide are interferences in Method 9010.

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.

3.6 Fatty acids, detergents, surfactants, and other compounds may cause foaming during the distillation when they are present in high concentrations and may make the endpoint for the titrimetric determination difficult to detect. Refer to Sec. 6.8 for an extraction procedure to eliminate this interference.

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 Hot plate stirrer/heating mantle.

4.3 pH meter.

4.4 Amber light.

4.5 Vacuum source.

4.6 Refrigerator.

4.7 Erlenmeyer flask - 500 mL.

4.8 KI starch paper.

4.9 Class A volumetric flasks-1000,250, and 100 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 $NaAsO_2$ 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 Section 5.3.1.

5.4.4 Potassium iodide starch paper.

5.5 Reagents for distillation

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

5.5.2 Bismuth nitrate (0.062M), $Bi(NO)_3 \bullet 5H_2O$. Dissolve 30 g $Bi(NO)_3 \bullet 5H_2O$ 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), $MgCl_2 \bullet 6H_2O$. Dissolve 510 g of $MgCl_2 \bullet 6H_2O$ in 1 liter of water.

5.5.6 Lead acetate paper.

5.5.7 Stock potassium cyanide solutions - Refer to Method 9014 for the preparation of stock cyanide solutions and calibration standards.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

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

6.3 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.

6.4 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.

6.5 Samples should be chilled to 4°C.

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

6.7 Solid and oily wastes may be extracted prior to analysis by method 9013. It uses a dilute NaOH solution (pH = 12) as the extractant. This yields extractable cyanide.

6.8 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.

<u>CAUTION</u>: 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.

<u>CAUTION</u>: 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 Analyze the total cyanide concentration of both the chlorinated and the unchlorinated samples by Method 9014 or 9213. The difference between the total cyanide concentration in the chlorinated and unchlorinated samples is equal to the cyanide amenable to chlorination.

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 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.

7.2.4 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.

7.2.5 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.

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

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

7.2.8 Proceed to the cyanide determinative methods given in Methods 9014 or 9213. If the distillates are not analyzed immediately, they should be stored at 4°C in tightly sealed flasks.

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 reagent blank per analytical batch or one in every 20 samples to determine if contamination or any memory effects are occurring.

8.3 Analyze check standards with every analytical batch of samples. If the standards are not within 15% of the expected value, then the samples must be reanalyzed.

8.4 Run one replicate sample for every 20 samples. A replicate sample is a sample brought through the entire sample preparation and analytical process. The CV of the replicates should be 20% or less. If this criterion is not met, the samples should be reanalyzed.

8.5 Run one matrix spiked sample every 20 samples to check the efficiency of sample distillation by adding cyanide from the working standard or intermediate standard to 500 mL of sample to ensure a concentration of approximately 40 µg/L. The matrix spiked sample is brought through the entire sample preparation and analytical process.

8.6 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.

8.7 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 The titration procedure using silver nitrate is used for measuring concentrations of cyanide exceeding 0.1 mg/L. The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

9.2 EPA Method 335.2 (sample distillation with titration) reports that in a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.06 to 0.62 mg/L CN^-, the standard deviations for precision were ± 0.005 to ± 0.094, respectively. In a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/L CN^-, recoveries (accuracy) were 85% and 102%, respectively.

9.3 In two additional studies using surface water, ground water, and landfill leachate samples, the titration procedure was further evaluated. The concentration range used in these studies was 0.5 to 10 mg/L cyanide. The detection limit was found to be 0.2 mg/L for both total and amenable cyanide determinations. The precision (CV) was 6.9 and 2.6 for total cyanide determinations and 18.6 and 9.1 for amenable cyanide determinations. The mean recoveries were 94% and 98.9% for total cyanide, and 86.7% and 97.4% for amenable cyanide.

10.0 REFERENCES

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FIGURE 1.
APPARATUS FOR CYANIDE DISTILLATION

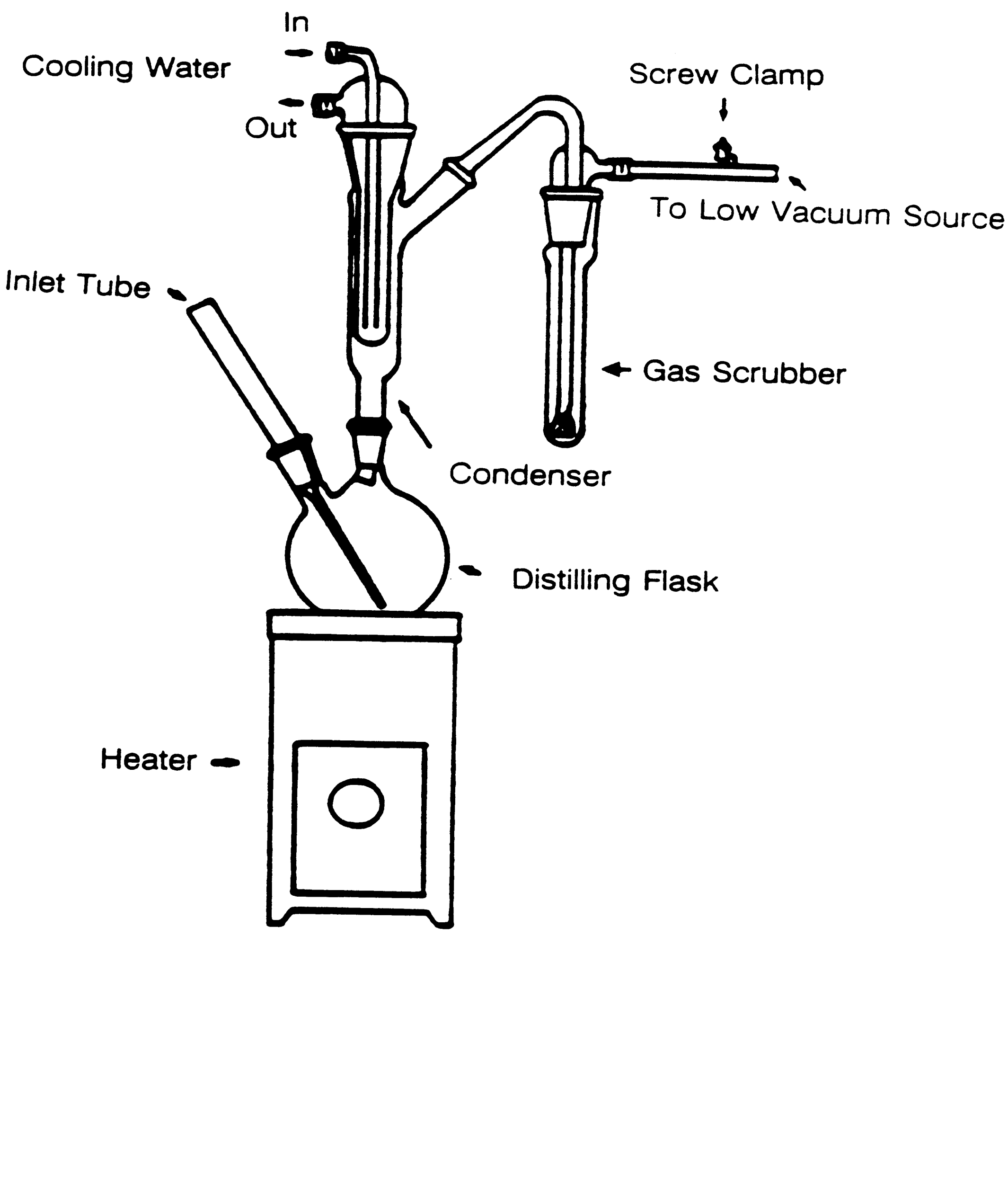
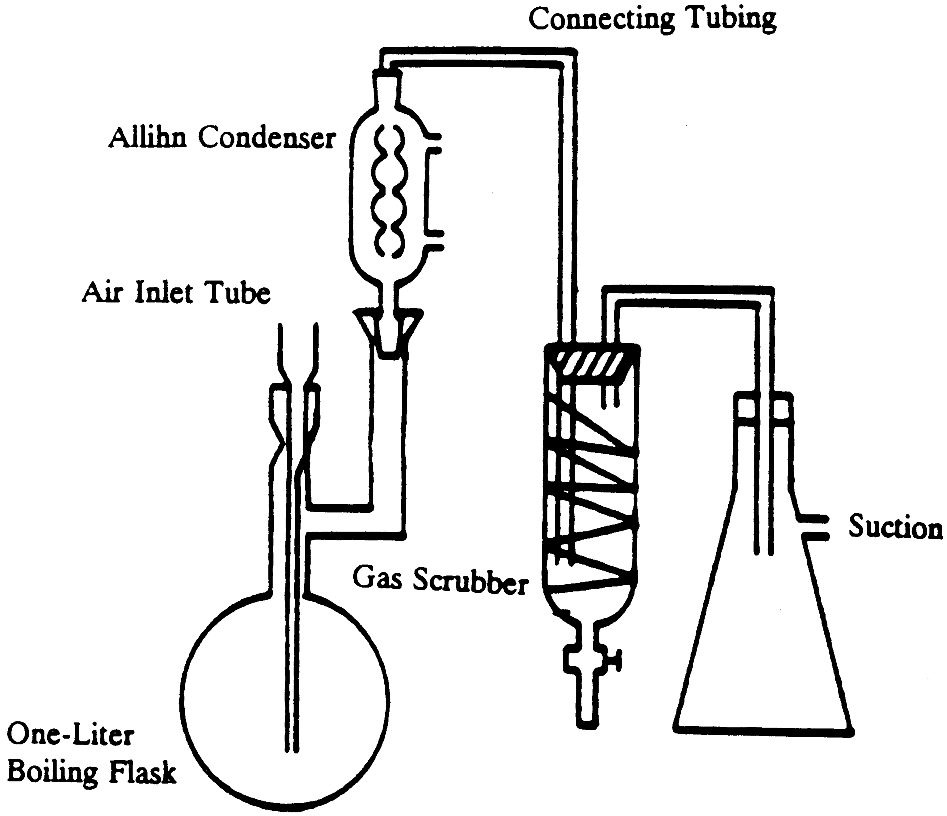


FIGURE 2.
APPARATUS FOR CYANIDE DISTILLATION



METHOD 9010B

TOTAL AND AMENABLE CYANIDE: DISTILLATION