METHOD #: 335.2 Approved for NPDES (Technical Revision 1980)

TITLE: Cyanide, Total (Titrimetric; Spectrophotometric)

ANALYTE: CN Cyanide

INSTRUMENTATION: Spectrophotometer

STORET No. 00720

1.0 Scope and Application

1.1 This method is applicable to the determination of cyanide in drinking, surface and saline waters, domestic and industrial wastes.

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

1.3 The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

2.0 Summary of Method

2.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of, a reflux-distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by volumetric titration or colorimetrically.

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-pyrazolone or pyridine-barbituric acid reagent. The absorbance is read at 620 nm when using pyridine-pyrazolone or 578 nm for pyridine-barbituric acid. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.3 The titrimetric measurement uses standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3.0 Definitions

3.1 Cyanide is defined as cyanide ion and complex cyanides converted to hydrocyanic acid (HCN) by reaction in a reflux system of a mineral acid in the presence of magnesium ion.

4.0 Sample Handling and Preservation

4.1 The sample should be collected in plastic or glass bottles of 1 liter or larger size. All bottles must be thoroughly cleansed and thoroughly rinsed to remove soluble material from containers.

4.2 Oxidizing agents such as chlorine decompose most of the cyanides. 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 0.06 g of ascorbic acid for each liter of sample volume.

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

4.4 Samples should be analyzed as rapidly as possible after collection. If storage is required, the samples should be stored in a refrigerator or in an ice chest filled with water and ice to maintain temperature at 4°C.

5.0 Interferences

5.1 Interferences are eliminated or reduced by using the distillation procedure described in Procedure 8.1, 8.2 and 8.3.

5.2 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 optional procedure described in Procedure 8.2. The apparatus for this procedure is shown in Figure 3.

5.3 Fatty acids will distill and form soaps under the alkaline titration conditions, making the end point almost impossible to detect.

5.3.1 Acidify the sample with acetic acid (1 + 9) to pH 6.0 to 7.0.

Caution: This operation must be performed in the hood and the sample left there until it can be made alkaline again after the extraction has been performed.

5.3.2 Extract with iso-octane, hexane, or chloroform (preference in order named) with a solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the fatty acids 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 NaOH solution.

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

6.0 Apparatus

6.1 Reflux distillation apparatus such 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.

6.2 Microburet, 5.0 mL (for titration).

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

6.4 Reflux distillation apparatus for sulfide removal as shown in Figure 3. The boiling flask same as 6. 1. The sulfide scrubber may be a Wheaton Bubber #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 should be fritted.

6.5 Flow meter, such as Lab Crest with stainless steel float (Fisher 11-164-50).

7.0 Reagents

7.1 Sodium hydroxide solution, 1.25N: Dissolve 50 g of NaOH in distilledwater, and dilute to 1 liter with distilled water.

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

7.5 Sulfuric acid; 18N: Slowly add 500 mL of concentrated H_2SO_4 to 500 mL of distilled water.

7.6 Sodium dihydrogenphosphate, 1 M: Dissolve 138 g of NaH2PO4*H2O in 1 liter of distilled water. Refrigerate this solution.

7.7 Stock cyanide solution: Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of distilled water. Standardize ù with 0.0192 N AgNO3. Dilute to appropriate concentration so that 1 mL = 1 mg CN.

7.8 Standard cyanide solution, intermediate: Dilute 100.0 mL of stock (1 mL = 1 mg CN) to 1000 mL with distilled water (1 mL = 100.0 ug).

7.9 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.

7.10 Standard silver nitrate solution, 0.0192 N: Prepare by crushing approximately 5 g AgNO3 crystals and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$, dissolve in distilled water, and dilute to 1000 mL (1 mL = 1 mg CN).

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

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

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

7.13.1 Pyridine-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 distilled water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.13.2 Pyridine-pyrazolone solution:

7.13.2.1 3-Methyl-1-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, heat to 60°C with stirring. Cool to room temperature.

7.13.2.2 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.

7.13.2.3 Pour solution (7.13.2.1) through non-acid-washed filter paper. Collect the filtrate. Through the same filter paper pour solution (7.13.2.2) collecting the filtrate in the same container as filtrate from (7.13.2.1). 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.

7.14 Magnesium chloride solution: Weight 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000 mL flask, dissolve and dilute to 1 liter with distilled water.

7.15 Sulfamic acid.

8.0 Procedure

8.1 For samples without sulfide.

8.1.1 Place 500 mL of sample, or an aliquot diluted to 500 mL in the 1 liter boiling flask. Pipet 50 mL of sodium hydroxide (7.1) 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 in the train. (Figure 1 or 2).

8.1.2 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 enters the boiling flask through the air inlet tube. Proceed to 8.4.

8.2 For samples that contain sulfide.

8.2.1 Place 500 mL of sample, or an aliquot diluted to 500 mL in the 1 liter boiling flask. Pipet 50 mL of sodium hydroxide (7.1) to the absorbing tube. Add 25 mL of lead acetate (7.2) to the sulfide scrubber.Connect the boiling flask, condenser, scrubber and absorber in the train. (Figure 3) The flow meter is connected to the outlet tube of the cyanide absorber.

8.2.2 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 enters 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 8.4.

8.3 If samples contain NO_3, and or NO_2 add 2 g of sulfamic acid solution (7.15) after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of H_2SO_4.

8.4 Slowly add 50 mL 18N sulfuric acid (7.5) through the air inlet tube. Rinse the tube with distilled water and allow the airflow to mix the flask contents for 3 min. Pour 20 mL of magnesium chloride (7.14) into the air inlet and wash down with a stream of water.

8.5 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, disconnect absorber and close off the vacuum source.

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

8.7 Withdraw 50 mL or less of the solution from the flask and transfer to a 100 mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25N sodium hydroxide solution (7.4). Add 15.0 mL of sodium phosphate solution (7.6) and mix.

8.7.1 Pyridine-barbituric acid method: Add 2 mL of chloramine T (7.12) and mix. See Note 1. After 1 to 2 minutes, add 5 mL of pyridine-barbituric

acid solution (7.13.1) and mix. Dilute to mark with distilled water and mix again. Allow 8 minutes for color development then read absorbance at 578 nm in a 1 cm cell within 15 minutes.

8.7.2 Pyridine-pyrazolene method: Add 0.5 mL of chloramine T (7.12) and mix. See Note 1 and 2. After 1 to 2 minutes add 5 mL of pyridine-pyrazolone solution (7.13.1) and mix. Dilute to mark with distilled water and mix again. After 40 minutes read absorbance at 620 nm in a 1 cm cell.

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 chlorine T. After one minute, recheck the sample.

NOTE 2: More than 05. mL of chloramine T will prevent the color from developing with pyridine-pyrazolone.

8.8 Standard curve for samples without sulfide.

8.8.1 Prepare a series of standards by pipeting suitable volumes of standard solution (7.9) into 250 mL volumetric flasks. To each standard add 50 mL of 1.25 N sodium hydroxide and dilute to 250 mL with distilled water. Prepare as follows:

ML of Working Standard Solution (1 mL = 10 μg CN)	Conc. μg CN per 250 mL
0	BLANK
1.0	10
2.0	20
5.0	50
10.0	100
15.0	150
20.0	200

8.8.2 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 low) be distilled and compared to similar values on the curve to insure 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.

8.8.3 Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations.

8.8.4 To check the efficiency of the sample distillation, add an increment of cyanide from either the intermediate standard (7.8) or the working standard (7.9) to 500 mL of sample to insure a level of 20 μg/L. Proceed with the analysis as in Procedure (8.1.1).

8.9 Standard curve for samples with sulfide.

8.9.1 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.

8.9.2 Prepare a standard curve by plotting absorbance of standard vs.

cyanide concentrations.

8.10 Titrimetric method.

8.10.1 If the sample contains more than 1 mg/L of CN, transfer the distillate or a suitable aliquot diluted to 250ml, to a 500 mL Erlenmeyer flask. Add lO-12 drops of the benzalrhodanine indicator.

8.10.2 Titrate with standard silver nitrate to the first change in color from yellow to brownish-pink. Titrate a distilled water blank using the same amount of sodium hydroxide and indicator as in the sample.

8.10.3 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.

9.0 Calculation

9.1 If the colorimetric procedure is used, calculate the cyanide, in μg/L, in the original sample as follows:

$$CN,\ \mu g/L = \frac{A \times 1{,}000}{B} \times \frac{50}{C}$$

where:

A = μg CN read from standard curve
B = mL of original sample for distillation
C = mL taken for colorimetric analysis

9.2 Using the titrimetric procedure, calculate concentration of CN as follows:

$$CN,\ mg/L = \frac{(A - B)1{,}000}{mL\ orig.\ sample} \times \frac{250}{mL\ of\ aliquot\ titrated}$$

where:

A = volume of $AgNO_3$ for titration of sample.
B = volume of $AgNO_3$ for titration of blank.

10.0 Precision and Accuracy

10.1 In a single laboratory (EMSL), using mixed industrial and domestic waste samples at concentrations of 0.06, 0.13, 0.28 and 0.62 mg/L CN, the standard deviations were ±0.005, ±0.007, ±0.031 and ±0.094, respectively.

10.2 In a single laboratory (EMSL), using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/L CN, recoveries were 85% and 102%, respectively.

Bibliography

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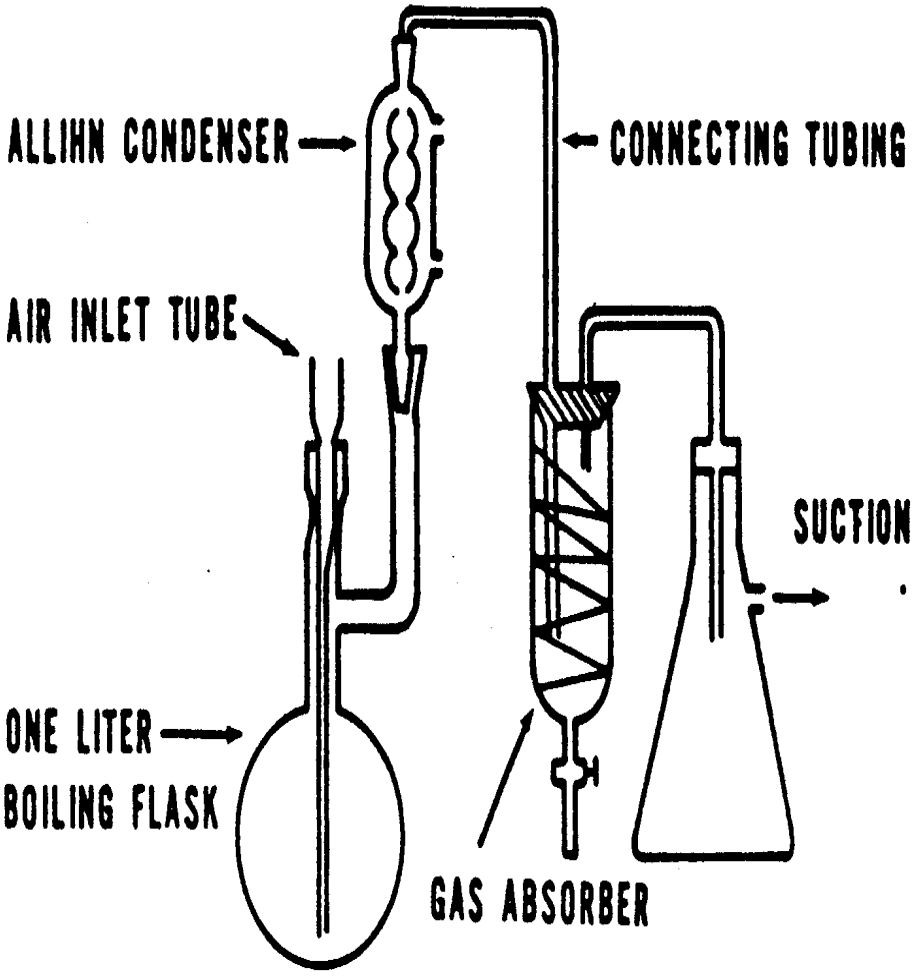

FIGURE 1

CYANIDE DISTILLATION APPARATUS

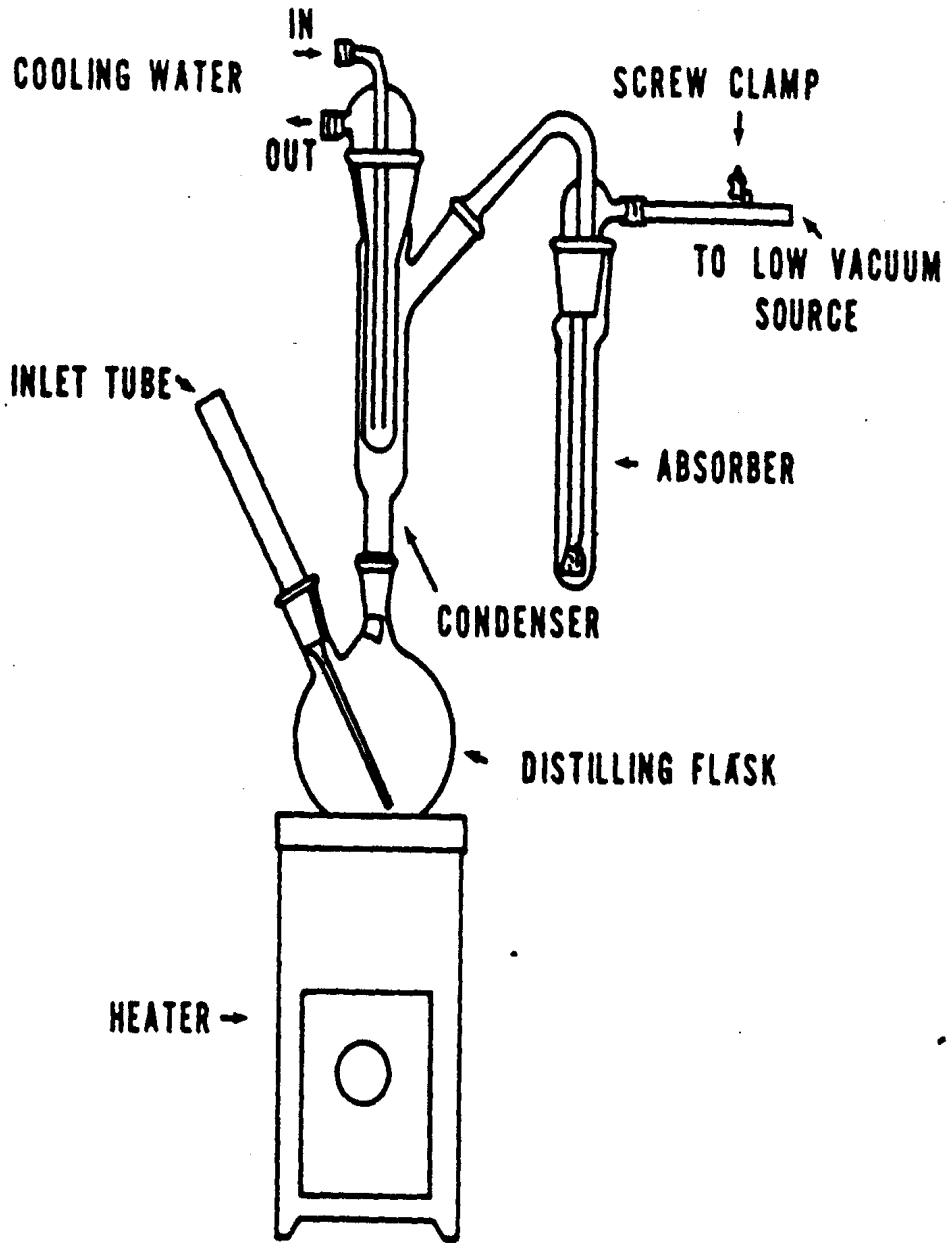

FIGURE 2

CYANIDE DISTILLATION APPARATUS

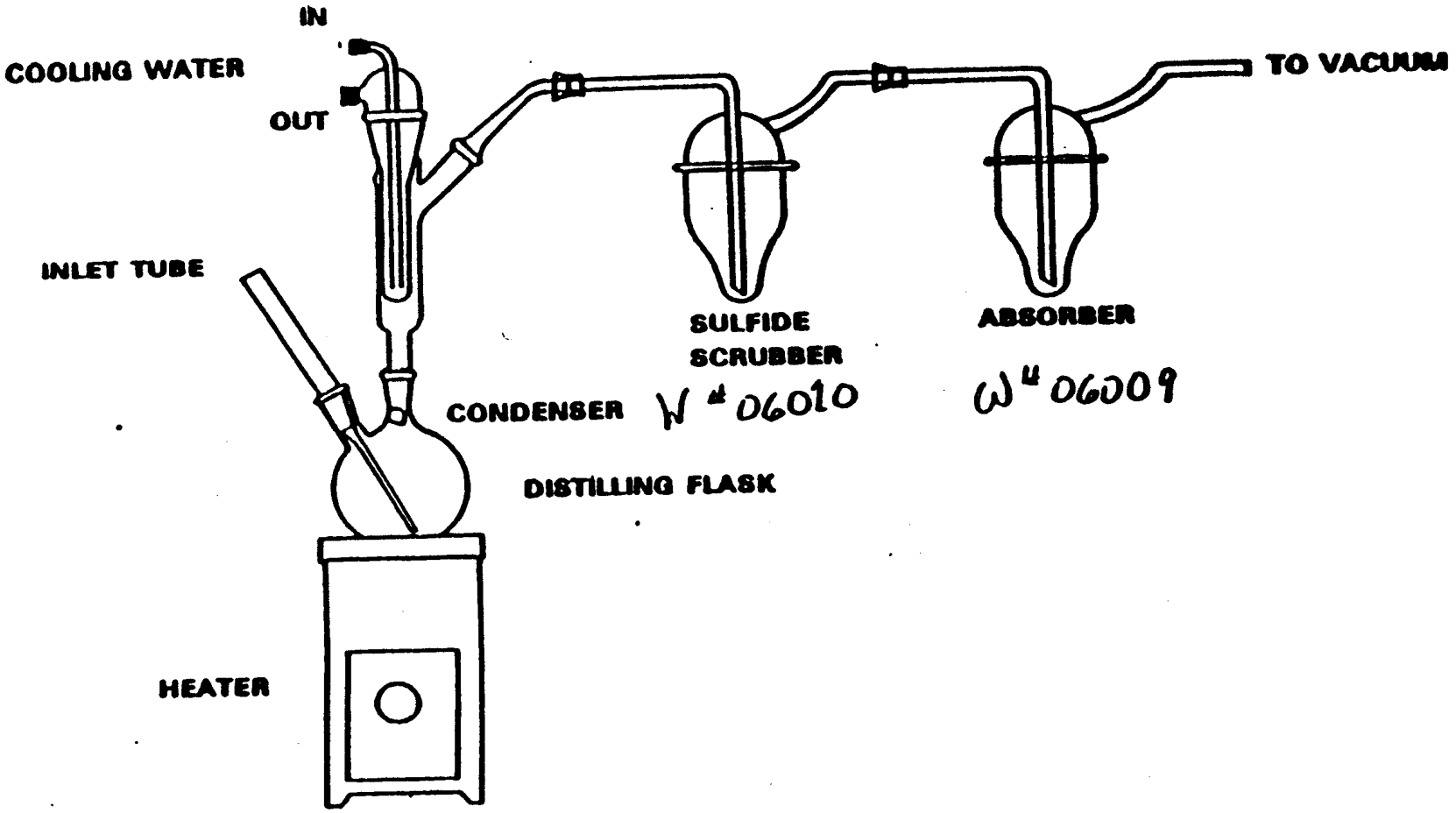

Figure 3.
Cyanide Distillation Apparatus