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WEST VALLEY NUCLEAR SERVICES CO., INC.

ANALYTICAL CHEMISTRY METHOD
ANALYTICAL AND PROCESS CHEMISTRY

ACM-CN-3501, Rev. 1
Effective Date: 06/28/89

SELECTIVE ELECTRODE DETERMINATION OF CYANIDE

Approved by:

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Analytical Chemistry

Part I

1.0 PURPOSE

This method will be used to quantitatively test an aqueous sample for cyanide.

2.0 APPLICATION

This method is designed to accurately analyze a sample for cyanide by using a distillation method followed by a potentiometric determination.

3.0 DISCUSSION

3.1 Hydrogen cyanide (HCN) is liberated from an acidified sample by distillation and purging with air. The HCN gas is collected by passing it through an NaOH scrubbing solution. Cyanide concentration in the scrubbing solution is determined by the potentiometric procedure.

3.2 CN^- in the alkaline distillate from the preliminary treatment procedures can be determined potentiometrically by using a CN^--selective electrode in combination with a double-junction reference electrode and a pH meter having an expanded millivolt scale, or a specific ion meter. This method can be used to determine CN^- concentration in place of either the colorimetric or titrimetric procedures in the concentration range of 0.05 to 10 mg CN^-/L.

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4.0 REFERENCES

Standard methods for the examination of water and waste water, 16th Edition, 412B Total Cyanide After Distillation and 412E Cyanide-Selective Electrode Method.

Part II

5.0 EQUIPMENT

NOTE: All calibrated equipment is to comply with ACP 7.1.

5.1 Boiling flask, 1 L, with inlet tube and provision for water-cooled condenser.

5.2 Gas absorber, with gas dispersion tube equipped with medium-porosity fritted outlet.

5.3 Heating element, adjustable.

5.4 Ground glass ST joints, TFE-sleeved or with an appropriate lubricant for the boiling flask and condenser. Neoprene stopper and plastic threaded joints also may be used.

5.5 Expanded-scale pH meter or specific-ion meter.

5.6 Cyanide-ion selective electrode.

5.7 Reference electrode, double-junction.

5.8 Magnetic mixer with TFE-coated stirring bar.

5.9 Assorted glassware.

6.0 REAGENTS AND STANDARDS

NOTE: (1) Unless otherwise stated prepare all reagents with ASTM Type II water.

NOTE: (2) All reagents and solutions are prepared per ACP 8.1 and have a shelf life of one year unless otherwise stated.

6.1 Sodium hydroxide solution: Dissolve 40g NaOH in water and dilute to 1L.

6.2 Magnesium chloride reagent: Dissolve 510g $MgCl_2.6H_2O$ in water and dilute to 1 L.

6.3 Sulfuric acid, H_2SO_4, 1+1.

6.4 Sodium hydroxide diluent: Dissolve 1.6g NaOH in water and dilute to 1L.

6.5 Stock cyanide solution: Dissolve approximately 1.6g NaOH and 2.51g KCN in 1 L distilled water. (CAUTION-KCN is highly toxic; avoid contact or inhalation.) 1 mL=1mg CN^-

6.6 Intermediate standard cyanide solution: Dilute a calculated volume (approximately 100 mL) of stock KCN solution, based on the determined concentration, to 1000 mL with NaOH diluent. Mix thoroughly; 1 mL=100 µg CN^-.

> 6.7 Dilute standard cyanide solution: Dilute 100 mL intermediate standard CN^- solution to 1000 mL with NaOH diluent; 1.00 mL=10.0 µg CN^-. Prepare daily and keep in a dark, glass-stoppered bottle.

7.0 SAFETY PRECAUTIONS

7.1 Cyanide is a very toxic chemical in its solid, liquid and gaseous state. Caution should be used when handling this substance. Cyanide should be handled in a vented hood when at all possible.

7.2 Observe standard laboratory safety procedures (ACP 7.2).

8.0 RECORDS

8.1 All measurement data and sample identification shall be recorded on the worksheet (Attachment A). The final result shall be recorded on the Analytical Request Sheet (ACP 5.1).

9.0 CALIBRATION AND CONTROL

9.1 A QC standard shall be analyzed and the results recorded in a QC log book per ACP 8.1. If the results are more than two standard deviations, the test will be repeated. If a test fails the second time, the method is out of control, the manager of Analytical Chemistry will be notified, and an investigation as to why the method is out of control will be initiated.

9.2 A spike shall be added to a duplicate sample to assure proper calibration and recovery of the spike. 0.1 mg/L low CN^- samples 1.0 mg/L for high CN^- samples.

10.0 PROCEDURE

> 10.1 Add up to 500 mL sample, containing not more than 10 mg CN^-/L (diluted if necessary with distilled water) to the boiling flask.

> Add 50 mL NaOH solution to the gas absorber and dilute, if necessary, with distilled water to obtain an adequate liquid depth in the absorber. Do not use more than 225 mL total volume of

absorber solution. Connect the train, consisting of boiling flask air inlet, flask, condenser, gas absorber suction flask trap, and aspirator. Adjust suction so that approximately three air bubble/s enters the boiling flask. This air rate will carry HCN gas from flask to absorber and usually will prevent a reverse flow of HCN through the air inlet. If this air rate does not prevent sample backup in the delivery tube, increase air-flow rate to four air bubbles/s. Observe air purge rate in the absorber where the liquid level should be raised not more than 6.5 to 10 mm. Maintain air flow throughout the reaction.

10.2 Carefully add 50 mL of 1+1 H_2SO_4 through the air inlet tube. Rinse tube with distilled water and let air mix flask contents for three minutes. Add 20 mL $MgCl_2$ reagent through air inlet and wash down with stream of water. A precipitate that may form redissolves on heating.

> 10.3 Heat with rapid boiling, but do not flood condenser inlet or permit vapors to rise more than halfway into condenser. Adequate refluxing is indicated by a reflux rate of 40 to 50 drops per minute from the condenser lip. Reflux for at least one hour. Discontinue heating but continue air flow. Cool for 15 minutes and drain gas washer contents into a separate container. Rinse connecting tube between condenser and gas washer with distilled water, add rinse water to drained liquid, and dilute to 100 mL in a volumetric flask..

10.4 CALIBRATION

> Use the dilute and intermediate standard CN^- solutions and the NaOH diluent to prepare a series of three standards, 0.1, 1.0, and 10.0 mg CN^-/L. Transfer approximately 50 mL of each of these standard solutions into a 100-mL beaker prerinsed with a small portion of standard being tested. Immerse CN^- and double-junction reference electrodes. Mix well on a magnetic stirrer at 25°C, maintaining as closely as possible the same stirring rate for all solutions.

Always progress from the lowest to the highest concentration of standard because otherwise equilibrium is reached only slowly. The electrode membrane dissolves in solutions of high CN^- concentration; do not use with a concentration above 10 mg/L. After making measurements remove electrode and soak in water.

> After equilibrium is reached (at least five minutes and not more than ten minutes), record potential (millivolt) readings and plot CN^- concentrations versus readings on semilogarithmic graph paper or use reqlm selective ion electrode curve utility to generate the graph. A straight line with a slope of approximately 59 mV per decade indicates that the instrument and electrodes are operating properly. The slope may vary somewhat from the theoretical value of 59.2 mV per decade because of manufacturing variation and

reference electrode (liquid-junction) potentials. The slope should be a straight line and is the basis for calculating sample concentration.

10.5 MEASUREMENT OF SAMPLE

> Place 50 mL of absorption liquid obtained in Section 10.3 into a 100-mL beaker. When measuring low CN^- concentrations, first rinse beaker and electrodes with a small volume of sample. Immerse CN^- and double-junction reference electrodes and mix on a magnetic stirrer at the same stirring rate used for calibration. After equilibrium is reached (at least five minutes and not more than 10 minutes), record values indicated on ion meter or found from graph prepared as above.

11.0 CALCULATIONS

$$\text{mg } CN^-/L = \frac{A \times B}{C}$$

where:

A = mg CN^-/L found from meter reading or graph

B = total volume of absorption solution after dilution, mL, and

C = volume of original sample used in the distillation, mL.

12.0 ATTACHMENT

Attachment A - Cyanide Worksheet (Selective Electrode)

ATTACHMENT A

SELECTIVE ELECTRODE CYANIDE WORKSHEET

SAMPLE NAME _____ LOG NUMBER _____

DISTILLED STANDARD= _____

INSTRUMENT USED: _____

SAMPLE IDENTIFICATION	BLANK					DISTILLED STD.		SPIKE
CONCENTRATION FACTOR						//////////		
mV READ						//////////		
PPM READ FROM GRAPH								
PPM/CONCENTRATION FACTOR								
% RECOVERY								

CONC.	mV	
STANDARD #1		
STANDARD #2		
STANDARD #3		
STANDARD #4		
STANDARD #5		

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PHOSPHATE - PHOTOMETRIC

Approved by:

C. W. McVay, Manager
Analytical and Process Chemistry

CANCELLED

ACM-PO_4-3601 was cancelled
because it no longer applies.

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