

METHOD 9213

POTENTIOMETRIC DETERMINATION OF CYANIDE IN AQUEOUS SAMPLES AND DISTILLATES WITH ION-SELECTIVE ELECTRODE

1.0 SCOPE AND APPLICATION

1.1 This method can be used for measuring free (non-complexed) cyanide and hydrocyanic acid in drinking waters, natural surface waters, domestic and industrial wastewaters, and in soil extracts (ASTM methods D4646-87, D5233-92 or D3987-85). The method may also be used as the determinative step for total cyanide in distillate following the distillation in Method 9010.

1.2 The method detection limit is 0.05 mg/L. Cyanide concentrations from 0.01 to 10 mg/L may be measured. However, using a linear calibration, results less than 0.05 mg/L may be biased up to approximately 120 percent high.

1.3 ISEs must be used carefully, and results must be interpreted cautiously, since an ISE may be affected by numerous analytical interferences which may either increase or decrease the apparent analyte concentration, or which may damage the ISE. Effects of most interferences can be minimized or eliminated by adding appropriate chemical reagents to the sample. Obtaining the most accurate results, therefore, requires some knowledge of the sample composition.

NOTE: ISE manufacturers usually include a list of interferences in the instruction manual accompanying an ISE, along with recommended methods for minimizing or eliminating effects of these interferences.

1.4 The cyanide ISE should not be used in solutions containing more than 30 mg/L of free cyanide, because such solutions will dissolve the ISE sensor silver compounds.

2.0 SUMMARY OF METHOD

2.1 Cyanide is determined potentiometrically using a cyanide ion-selective electrode (ISE) in conjunction with a double-junction reference electrode and a pH meter with an expanded millivolt scale or an ISE meter capable of being calibrated directly in terms of cyanide concentration.

2.2 Standards and samples are mixed 100:1 with an ionic strength adjustment solution (ISA). Calibration is performed by analyzing a series of standards and plotting mV vs. cyanide concentration on semilog paper or by calibrating the ion meter directly in terms of cyanide concentration.

3.0 INTERFERENCES

3.1 Transition metal cations interfere by forming very stable complexes with cyanide which are not measured by the cyanide ISE. For example, copper(II) ions interfere with the cyanide determination by oxidizing cyanide to cyanogen gas and precipitating copper(I) cyanide. Because these complexes are very stable and their rate of dissociation is slow (days) at room temperature (25°C), this method is restricted to the analysis of free cyanide and hydrocyanic acid in undistilled samples. Total cyanide may be determined in samples distilled as per Method 9010. (Distillation removes interferants and breaks down metal-analyte complexes and insoluble salts.)

3.2 Several anions and one acid were tested for cyanide interference. (See Table 1.) As shown, hydrogen ions (acid) interfere by forming hydrocyanic acid. Hydrogen ions are removed by adding ISA.

3.3 Sulfide interferes with the determination by reacting directly with the ISE. This interference can be removed after adding ISA by adding and well mixing small amounts (about 0.05 g) of powdered lead carbonate until the added powder remains white.

3.4 Temperature changes affect electrode potentials. Using an ISE calibrated at 22°C, a 1.00 mg/L cyanide solution was measured as 0.98 mg/L at 22 °C and 0.64 mg/L at 32 °C (see Ref. 3). Therefore, standards and samples must be equilibrated at the same temperature ($\pm 1^\circ\text{C}$).

3.5 The user should be aware of the potential of interferences from colloidal substances and that, if necessary, the samples may be filtered.

4.0 APPARATUS AND MATERIALS

4.1 pH/mV meter capable of reading to 0.1 mV or an ISE meter.

4.2 Cyanide ISE (Orion 9406 or equivalent) and double-junction reference electrode (Orion 9002 or equivalent).

4.3 Thermally isolated magnetic stirrer, polytetrafluoroethylene (PTFE)-coated stir bar, and stopwatch.

4.4 Volumetric flask, 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 ISA solution (10M NaOH): Dissolve 40 g of sodium hydroxide in sufficient reagent water to make 100 mL of solution. Cool, and store in a polyethylene bottle.

CAUTION: This solution is extremely corrosive.

5.4 Powdered lead carbonate $[(\text{PbCO}_3)_2 \cdot \text{Pb}(\text{OH})_2]$: Use in approximately 0.05 g increments to remove sulfide interference. (See Section 3.3.)

5.5 Cyanide calibration stock solution (1,000 mg/L CN⁻): Dissolve 0.2504 g of potassium cyanide (dried two hours at 110°C and stored in a desiccator) in reagent water, add 1.0 mL of ISA and dilute to 100.0 mL in a volumetric flask. Store in a clean bottle.

5.6 Cyanide standard solution (100.0 mg/L CN⁻): Dilute 10.00 mL of 1,000 mg/L cyanide calibration stock solution to 100.0 mL with reagent water in a volumetric flask.

5.7 Cyanide calibration standards: Prepare a series of calibration standards by diluting the 100.0 mg/L cyanide standard. A suitable series is given in the table below.

mL of 100.0 mg/L CN ⁻ Solution	Concentration when Diluted to 50.0 mL (mg/L CN ⁻)
0.0150	0.0300
0.0500	0.100
0.150	0.300
0.500	1.00
1.50	3.00

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

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 must be preserved by adding 50% sodium hydroxide until the pH is greater than or equal to 12 at the time of collection and should be chilled to 4°C. When properly preserved, cyanide samples can be stored for up to 14 days prior to analysis.

7.0 PROCEDURE

7.1 Calibration

7.1.1 When using a cyanide ISE and a separate double-junction reference electrode, ensure that reference electrode inner and outer chambers are filled with solutions recommended by the manufacturer. Equilibrate the electrodes for at least one hour in a 0.300 mg/L cyanide standard before use.

7.1.2 Calibrate the cyanide ISE using standards that narrowly bracket the expected sample concentration. If the sample concentration is unknown, calibrate with 0.100 mg/L and 1.00 mg/L cyanide standards. Add 50.0 mL of standard and 0.50 mL of ISA to a 100 mL beaker. Add a PTFE-coated magnetic stir bar, place the beaker on a magnetic stir plate, and stir at slow speed (no visible vortex). Immerse the electrode tips to just above the rotating stir bar. If using an ISE meter, calibrate the meter in terms of cyanide concentration following the manufacturer's instructions. If using a pH/mV meter, record the meter reading (mV) as soon as the reading is stable, but in no case should the time exceed five minutes after immersing the electrode tips. Prepare a calibration curve by plotting measured potential (mV) as a function of the logarithm of cyanide concentration. The slope must be 54-60 mV per decade of cyanide concentration. If the slope is not acceptable, the ISE may not be working properly. For corrective action, consult the ISE operating manual.

7.2 Allow samples and standards to equilibrate to room temperature.

7.3 Prior to and between analyses, rinse the electrodes thoroughly with reagent water and gently shake off excess water. Low-level measurements are faster if the electrode tips are first immersed five minutes in reagent water.

7.4 Add 50.0 mL of sample and 0.50 mL of ISA to a 100 mL beaker. Add a PTFE-coated magnetic stir bar. Place the beaker on a magnetic stir plate and stir at a slow speed (no visible vortex). Immerse the electrode tips to just above the rotating stir bar. Record the meter reading (mV or concentration) as soon as the reading is stable, but in no case should the time exceed five minutes after immersing the electrode tips. If reading mV, determine cyanide concentration from the calibration curve.

7.5 When analyses have been completed, rinse the electrodes thoroughly and store them in a 0.30 mg/L cyanide standard solution. If the electrodes will not be used more than one day, drain the reference electrode internal filling solutions, rinse with reagent water, and store dry.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Initial Calibration Verification standard (ICV): After performing the calibration step (7.1), verify calibration by analyzing an ICV. The ICV contains a known cyanide concentration at the mid-range of the calibration standards and is from an independent source. ICV recovery must be 90-110 percent. If not, the error source must be found and corrected. An acceptable ICV must be analyzed prior to sample analysis. The ICV also serves as a laboratory control sample.

8.3 Continuing Calibration Verification standard (CCV): After every 10 samples, and after the final sample, a CCV must be analyzed. The CCV contains a known cyanide concentration at mid-calibration range. CCV recovery must be 90-110 percent. If not, the error source must be found and corrected. If the ISE calibration has changed, all samples analyzed since the last acceptable CCV must be re-analyzed.

8.4 Reagent blank: After the ICV and after every CCV, a reagent blank must be analyzed. A reagent blank is reagent water mixed 100:1 with ISA. The indicated reagent blank concentration must be less than 0.03 mg/L cyanide. If not, the contamination source must be found and corrected. All samples analyzed since the last acceptable reagent blank must be re-analyzed.

8.5 Matrix spike: Follow the matrix spike protocols presented in Chapter One. The spike concentration must be 10 times the detection limit and the volume added must be negligible (less than or equal to one-thousandth the sample aliquot volume). Spike recovery must be 75-125 percent. If not, samples must be analyzed by the method of standard additions.

9.0 METHOD PERFORMANCE

9.1 In a single-laboratory evaluation, a series of standards with known cyanide concentrations was analyzed with a cyanide ISE. Measurements were obtained over three consecutive days using an Orion 9406 cyanide ISE and an Orion 9002 double-junction reference electrode connected to an Orion 940 ISE meter. A two-point calibration (0.20 and 2.0 mg/L cyanide) was performed prior to analysis. The results are listed in Table 2.

9.2 In the same study, three groundwater samples were spiked with cyanide at four different concentrations and were measured with the cyanide ISE. (The groundwater samples initially contained <0.1 mg/L cyanide.) Each spiked sample was analyzed at each concentration and the mean recoveries and RSDs are given in Table 3.

9.3 A 50g portion of soil, which initially contained <0.1 mg/kg cyanide, was spiked with 2.50 mg/kg cyanide to obtain an anion concentration in a single extract volume within the linear

range of the ISE. The extract was then analyzed for cyanide using this ISE method, and 92% of the soil spike was recovered.

10.0 REFERENCES

1. Franson, Mary Ann H., Ed. *Standard Methods for the Examination of Water and Wastewater*, 18th Edition. American Public Health Association, Washington, DC, 1992.
2. Model 94-06 Cyanide Electrode Instruction Manual. Orion Research, Inc., Boston, MA, 1986.
3. Miller, E.L., Waltman, D.W., and Hillman, D.C. Single-Laboratory Evaluation of Fluoride, Chloride, Bromide, Cyanide, and Nitrate Ion-Selective Electrodes for Use in SW-846 Methods. Lockheed Engineering and Sciences Company for Environmental Monitoring Systems Laboratory, U.S. EPA. September 1990. EPA/600/X-90/221.
4. Cotton, F. Albert, and Geoffrey Wilkinson; *Advanced Inorganic Chemistry, 2nd Edition*; Interscience Publishers, New York, NY; 1966.
5. Kolthoff, I.M., E.B. Sandell, E.J. Meehan, and Stanley Bruckenstein; *Quantitative Chemical Analysis, 4th Edition*; The MacMillan Company, New York, NY; 1969.

TABLE 1
CYANIDE ISE INTERFERENCES

Analyte Concentration (mg/L)	Interference	Measured Concentration (mg/L)	RSD (%)
0.200	None	0.201	1.0
2.00	None	2.00	0.7
2.00	0.01 M H ₂ SO ₄	<0.05	*
0.200	200 mg/L Cl ⁻	0.204	2.0
0.200	200 mg/L Br ⁻	0.200	2.7
2.00	20 mg/L S ⁻² + 0.05 g PbCo ₃	2.02	1.6
* Single Measurement			

TABLE 2
RESULTS FROM A SINGLE-LABORATORY ACCURACY
EVALUATION OF A CYANIDE ISE

Cyanide Concentration (mg/L)	Cyanide Detected (mg/L)	Cyanide Recovery (%)	Rel. Std. Deviation (%)
0.0100	0.0217	217	27
0.0200	0.0340	170	13
0.0500	0.0520	104	8
0.100	0.103	103	6
0.200	0.198	99	3
0.500	0.48	96	6
1.00	1.03	103	6
2.00	2.02	101	3
5.00	5.00	100	6
10.0	9.9	99	4

TABLE 3
MEAN SPIKE RECOVERIES OF CYANIDE IN
THREE GROUNDWATER SAMPLES

Analyte Spike Concentration (mg/L)	Spike Recovery (%)	Rel. Std. Deviation (%)
0.0500	115	22.3
0.150	103	7.6
0.300	98	8.3
1.00	103	1.1

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