



Standard Test Method for Determination of Metal Cyanide Complexes in Wastewater, Surface Water, Groundwater and Drinking Water Using Anion Exchange Chromatography with UV Detection¹

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1. Scope*

1.1 This test method covers the determination of the metal cyanide complexes of iron, cobalt, silver, gold, copper and nickel in waters including groundwaters, surface waters, drinking waters and wastewaters by anion exchange chromatography and UV detection. The use of alkaline sample preservation conditions (see 10.3) ensures that all metal cyanide complexes are solubilized and recovered in the analysis (1-3).²

1.2 Metal cyanide complex concentrations between 0.20 to 200 mg/L may be determined by direct injection of the sample. This range will differ depending on the specific metal cyanide complex analyte, with some exhibiting greater or lesser detection sensitivity than others. Approximate concentration ranges are provided in 12.2. Concentrations greater than the specific analyte range may be determined after appropriate dilution. This test method is not applicable for matrices with high ionic strength (conductivity greater than 500 meq/L as Cl) and TDS (greater than 30 000 mg/L), such as ocean water.

1.3 Metal cyanide complex concentrations less than 0.200 mg/L may be determined by on-line sample preconcentration coupled with anion exchange chromatography as described in 11.3. This range will differ depending on the specific metal cyanide complex analyte, with some exhibiting greater or lesser detection sensitivity than others. Approximate concentration ranges are provided in 12.2. The preconcentration method is not applicable for silver and copper cyanide complexes in matrices with high TDS (greater than 1000 mg/L).

1.4 The test method may also be applied to the determination of additional metal cyanide complexes, such as those of platinum and palladium. However, it is the responsibility of the user of this standard to establish the validity of the test method for the determination of cyanide complexes of metals other than those in 1.1.

¹ This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.05 on Inorganic Constituents in Water.

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² The boldface numbers in parentheses refer to the list of references at the end of this standard.

1.5 The presence of metal complexes within a sample may be converted to Metal CN complexes and as such, are altered with the use of this method. This method is not applicable to samples that contain anionic complexes of metals that are weaker than cyanide complexes of those metals.

1.6 The values stated in SI units are to be regarded as standard. The values given in parentheses are mathematical conversions to inch-pound units that are provided for information only and are not considered standard.

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, refer to Section 9.

2. Referenced Documents

2.1 ASTM Standards:³

- D1129 Terminology Relating to Water
- D1193 Specification for Reagent Water
- D2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D19 on Water
- D3370 Practices for Sampling Water from Closed Conduits
- D3856 Guide for Management Systems in Laboratories Engaged in Analysis of Water
- D5810 Guide for Spiking into Aqueous Samples
- D5847 Practice for Writing Quality Control Specifications for Standard Test Methods for Water Analysis
- D6696 Guide for Understanding Cyanide Species

3. Terminology

3.1 Definitions:

3.1.1 For a definition of terms used in this standard, refer to Terminology D1129.

3.2 Definitions of Terms Specific to This Standard:

³ For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

*A Summary of Changes section appears at the end of this standard

3.2.1 *anion exchange chromatography, n*—a type of liquid chromatography in which anionic analytes are separated by differential retention on an anion exchange resin and detected by an appropriate detection mechanism.

3.2.2 *eluent, n*—the liquid mobile phase used in anion exchange chromatography to transport the sample through the chromatography system.

3.2.3 *analytical column, n*—the chromatography column that contains the stationary phase for separation by ion exchange.

3.2.3.1 *Discussion*—The column is packed with anion exchange resin that separates the analytes of interest based on their retention characteristics prior to detection.

3.2.4 *guard column, n*—a short chromatography column that is placed before the analytical column to protect the latter from particulates and impurities that may cause fouling.

3.2.5 *anion trap column, n*—a high-capacity, low-pressure anion exchange column used to remove reagent impurities from the eluent stream.

3.2.5.1 *Discussion*—The anion trap column is placed between the eluent reservoir and the gradient pump.

3.2.6 *gradient elution, n*—a type of elution in which the eluent composition is steadily altered throughout the analysis in order to provide for an adequate separation of the analytes of interest prior to detection.

3.2.7 *gradient pump, n*—a liquid chromatography pump that is capable of performing gradient elutions.

3.2.8 *total cyanide, n*—the sum total of all of the inorganic chemical forms of cyanide.

3.2.8.1 *Discussion*—Total cyanide thus includes both free cyanide and anionic metal cyanide complexes.

3.2.9 *metal cyanide complex, n*—a negatively charged ionic complex consisting of one or more cyanide ions bound to a single transition metal cation.

3.2.9.1 *Discussion*—Also referred to as *metal-complexed cyanides*, these complexes have the general formula:



where:

M = transition metal cation,

b = number of cyanide groups, and

x = ionic charge of the transition metal complex.

3.2.9.2 *Discussion*—Metal cyanide complexes are relatively stable and require moderate to highly acidic conditions in order to dissociate and form free cyanide. Based on their stability, metal cyanide complexes are divided into two categories: “weak metal cyanide complexes” and “strong metal cyanide complexes.” Examples of strong metal cyanide complexes include the iron cyanide complexes prevalent in many cyanide containing industrial wastewaters. The iron cyanide complexes are considered to be among the most stable and least toxic forms of cyanide. Refer to Guide [D6696](#) for a more detailed discussion of aqueous cyanide species.

3.2.9.3 *Discussion*—The metal cyanide complexes can form

salts with a variety of alkali and transition metal cations. These alkali metal cyanide complex salts are soluble under alkaline conditions ([1-3](#)).

3.2.10 *free cyanide, n*—the form of cyanide recognized as being bioavailable and toxic.

3.2.10.1 *Discussion*—Free cyanide may be present as either molecular HCN or the anion CN⁻ depending on the pH conditions. Refer to Guide [D6696](#) for a more detailed discussion of aqueous cyanide species.

4. Summary of Test Method

4.1 Dissolved metal cyanide complexes are determined by anion exchange chromatography. For samples containing from 0.2 to 200 mg/L metal cyanides a sample volume of 0.1 mL is injected directly into the ion chromatograph where the metal cyanide analytes are separated by being differentially retained on the anion exchange column ([4](#)). The concentration range will differ depending on the specific metal cyanide analyte, with some complexes exhibiting greater or lesser detection sensitivity than others based on their molar absorptivity. Refer to [12.2](#) for actual concentration ranges for individual metal cyanide complexes. The metal cyanide complexes are eluted from the column by the eluent gradient and detected as signal peaks using UV absorption at 215 nm. Their concentrations in the sample are determined by comparison of the analyte peak area with a standard calibration plot. Under the alkaline conditions of the analysis, ferricyanide ($[Fe(CN)_6]^{3-}$) is reduced to ferrocyanide ($[Fe(CN)_6]^{4-}$) ([1, 2](#)), yielding a single analyte peak. Any unreduced ferricyanide will be exhibited as tailing on the ferrocyanide peak.

4.2 For samples containing from 0.50 to 200 µg/L, dissolved metal cyanide complexes are determined by using anion exchange chromatography coupled with on-line sample preconcentration ([4, 5](#)). Twenty mL of sample is passed through an anion exchange concentrator column. As the sample passes through the column, the metal cyanide complexes are retained and concentrated on the column while the remainder of the sample matrix is directed to waste. Following concentration, the metal cyanide analytes are eluted from the concentrator column through gradient elution, into the chromatograph and onto an anion exchange column where the remainder of the analysis is completed as described in [4.1](#). The calibration range for metal cyanide complexes using sample preconcentration method is between 0.50 to 200 µg/L. This range will differ depending on the specific metal cyanide analyte, with some complexes exhibiting greater or lesser detection sensitivity than others based on their molar absorptivity. Refer to [12.2](#) for actual concentration ranges for individual metal cyanide complexes.

5. Significance and Use

5.1 This method directly determines the concentration of metal cyanide complexes in environmental waters. The method is important from an environmental regulatory perspective because it differentiates metal cyanide complexes of lesser toxicity from metal cyanide complexes of greater toxicity. Previous determinations of strong metal cyanide complexes

assumed that the concentration of strong metal cyanide complexes is equivalent to the difference between the total cyanide and the free cyanide. This approach is subject to error because different methods used to determine free cyanide often provide widely varying results, thus impacting the strong metal cyanide complex concentration that is determined by difference. The direct analysis using anion exchange chromatography avoids these method biases and provides for a more accurate and precise determination of metal cyanide complexes.

6. Interferences

6.1 Photodecomposition of some metal cyanide complexes such as those of iron can reduce their concentration (6-8). Samples shall be collected so as to prevent exposure to light (see 10.2). Samples shall be analyzed in amber bottles and protected from light whenever possible.

6.2 Carbonate is not a method interference but can accumulate by adherence to the anion exchange resin of the analytical column. This may eventually lead to unstable baselines and a reduction in column capacity and analyte retention. Care shall be taken to avoid carbonate contamination when preparing and using sodium hydroxide eluents (9, 10). (**Warning**—Carbonate is formed in sodium hydroxide solutions by reaction with atmospheric carbon dioxide. Prepare all eluents using reagent water degassed by helium sparging or vacuum sonication to prevent carbonate contamination as well as eluent outgassing during the analysis. Guidelines are provided in the test method for preparing low-carbonate sodium hydroxide eluent and reagent solutions (see Refs 9, 10).)

6.3 Commercial grade sodium cyanide used in the preparation of Eluent 1 (see 8.12) often contains metal cyanide complex impurities. These impurities can cause noisy, unstable baselines during the gradient elution profile. The installation of an anion trap column between the Eluent 1 reservoir and the gradient pump removes the impurities from the eluent stream resulting in improved chromatographic baselines. Guidelines for preparing and installing the anion trap column are provided in the test method (see 7.1.6 and 11.6).

6.4 The IonPac⁴ AG5, AG11, AS5 and AS11 chromatography columns referenced in the test method (see 7.1.7, 7.1.8, and 7.2.4) are polymeric and accordingly will concentrate neutral organics and polyvalent organic anions at the head of the column. Organic species containing a carbonate functional group will absorb at 215 nm. These species can potentially cause “ghost” peaks when eluted during the analysis. This effect is a function of the quality of the water used in the preparation of the eluent solutions as well as the column equilibration time. Sample preconcentration will enhance this effect. High purity reagent water containing as low a concentration as possible of organic contaminants should be used in the preparation of reagents (see 8.2).

6.5 Free metal cations present in either the sample matrix or as impurities in the combined eluent stream can combine with the free cyanide present in Eluent 1 (see 8.12) to form extraneous metal cyanide complexes. Metal free trap columns

should be installed to prevent positive interference by extraneous metal cyanide complexes during the low-level analysis procedure (see 7.2.5).

6.6 The method calibration for iron cyanide is based on its reduced form, ferrocyanide. Although the alkaline conditions of the analysis favor the reduction of ferricyanide to ferrocyanide, any unreduced species could potentially contribute to a bias in the analytical results.

6.7 Matrices with relatively high ionic strength or high total dissolved solids, for example, ocean water, will affect the performance of the analytical columns, resulting in poor separation and recovery of the metal cyanide complexes.

6.8 When performing anion exchange chromatography coupled with on-line sample preconcentration, the silver and copper cyanide complexes exhibit reduced precision and increased bias, especially in high ionic strength matrices, for example, certain wastewaters. For the silver cyanide complex, large front-end tailing in samples containing high total dissolved solids affects peak resolution. For the copper and silver cyanide complexes possible dissociation during the analysis might also affect quantitation in samples containing high total dissolved solids. Any matrix with high ionic strength and total dissolved solids (TDS > 1000 mg/L) could affect the performance of the analytical columns when performing sample preconcentration, which may result in poor separation and recovery of metal cyanide complexes.

7. Apparatus

7.1 *Anion Exchange Chromatography Apparatus Requirements:*

7.1.1 *Pressurized Eluent Reservoir*—Accessories must include a gas regulator capable of maintaining a 13.8 to 68.9 kPa (2 to 10 psi) head pressure on the eluent solutions using helium gas.

7.1.2 *Pressurizable Eluent Bottles*—Bottles must be capable of withstanding an internal pressure of 51 to 68.9 kPa (7 to 10 psi). The bottles must be made of a chemically inert plastic such as polypropylene, suitable for use with sodium hydroxide-based eluents.

7.1.3 *Tubing*—To be used with the eluent reservoir and made of a material that is compatible with the eluent solutions.

7.1.4 *Gradient Pump*—High performance liquid chromatography (HPLC) or ion chromatography (IC) pump capable of delivering a constant flow in the range of 1 to 5 mL/min at a pressure of 1379 to 13790 kPa (200 to 2000 psi).

7.1.5 *Chromatography Tubing*—The tubing must be pressure resistant (approximately 20682 kPa {3000 psi}) and made of a material that is compatible with the eluent solutions. Examples of suitable materials are polyether ether ketone (PEEK) and 316 stainless steel.

7.1.6 *Anion Trap Column*—The anion trap column is a low pressure column that is placed between the Eluent 1 reservoir and the gradient pump inlet to trap and remove metal cyanide impurities. The column is packed with a high-capacity anion exchange resin. An example of a suitable column is the Dionex IonPac ATC-3 4-mm (9 by 24 mm) or equivalent (11). The

⁴ A trademark by Dionex Corporation, Sunnyvale, CA.