ASTM D7237 Standard Test Method for Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection

This is a new standard test method that was developed by ASTM Committee D19 to determine the concentration of free cyanide in an aqueous wastewater or effluents. The method detects free cyanide (HCN and CN^-) and a few weak metal-cyanide complexes (Zn and Cd) that are easily dissociated into free cyanide ions under the conditions of the test.

The treated sample is introduced into a flow injection analysis (FIA) system where it is mildly acidified at pH 6 - 8 in an effort to measure the hydrogen cyanide (HCN) that would be present in an aqueous environment. The method does not utilize ligand exchange reagents. Hydrogen cyanide gas diffuses from the acid stream through a hydrophobic gas diffusion membrane into an alkaline acceptor stream. The diffused cyanide passes through an amperometric flow cell. In the presence of cyanide, silver in the working electrode of the flow cell is oxidized at the applied potential. The anodic current measured is directly proportional to the concentration of cyanide.

ASTM D6888-09 Standard Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection

ASTM Committee D19 on Water has recently revised this standard. This method is used to determine the concentration of available inorganic cyanide in an aqueous wastewater or effluent. The method detects free cyanide (HCN and CN^-) and metal-cyanide complexes that are easily dissociated into free cyanide ions. The method does not detect the less toxic strong metal-cyanide complexes, known as total cyanide or cyanides that are not “amenable to chlorination.”

Complex cyanide bound with nickel or mercury is released by ligand displacement with the addition of a ligand displacement agent prior to analysis. Other available cyanide species do not require ligand displacement under the test conditions. The treated sample is introduced into a flow injection analysis (FIA) system where it is acidified to form hydrogen cyanide (HCN). The hydrogen cyanide gas diffuses from the acid stream through a hydrophobic gas diffusion membrane into an alkaline acceptor stream. A sulfide complex reagent removes up to 50-mg/L sulfide automatically. The diffused cyanide passes through an amperometric flow cell. In the presence of cyanide, silver in the working electrode of the flow cell is oxidized at the applied potential. The anodic current measured is directly proportional to the concentration of cyanide.

ASTM D2036-09 Standard Test Methods for Cyanides in Water, Test Method A Total Cyanide after Distillation

ASTM Committee D19 on Water has recently revised this standard. The method detects free cyanide (HCN and CN^-), weak to moderately strong metal-cyanide complexes, and strong-metal-cyanide complexes (e.g. iron cyanides) that dissociate and release free

cyanide when refluxed under strongly acidic conditions. The cyanide in complexes of some transition metals, for example, cobalt, gold, platinum, etc., is not determined.

Samples are digested with sulfuric acid in the presence of magnesium chloride in a distillation reaction vessel that consists of a 1-L round bottom flask, with provision for an inlet tube and a condenser connected to a vacuum-type absorber. The strongly acid sample is heated to boiling using an electric heater. Smaller distillation tubes such as 50-mL MIDI tubes or 6-mL MicroDist™ tubes described in D7284-08 can be used if the quality control requirements in D2036-09 are satisfied.

After distillation, the cyanide concentration can be determined by titration, ion chromatography, colorimetric procedure (spectrophotometrically), selective ion electrode, or flow injection analysis with gas diffusion separation and amperometric detection. The inclusion of ion chromatography and gas diffusion separation with amperometric detection as determinative steps (D2036-09, sections 16.5 and 16.6) gives users additional options to measure cyanide after distillation. Furthermore, ion chromatography and gas diffusion amperometry mitigate interferences that have been associated with conventional colorimetric test methods.

ASTM D7284-08 Standard Test Method for Total Cyanide in Water by Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection

This is a new standard test method that was developed by ASTM Committee D19 to determine the concentration of total cyanide in an aqueous wastewater or effluents. The method detects free cyanide (HCN and CN^-), weak to moderate metal-cyanide complexes, and strong-metal-cyanide complexes (e.g. iron cyanides) that dissociate and release free cyanide when refluxed under strongly acidic conditions. This procedure is applicable over a range of 2- 400 µg/L (parts per billion) total cyanide. Higher concentrations can be measured with sample dilution or lower injection volume. The determinative step of this method is flow injection with gas diffusion amperometric detection.

Prior to analysis, samples must be distilled with a micro-distillation apparatus described in the test method or with a suitable cyanide distillation apparatus specified in Test Methods D 2036-09. The samples are distilled with a strong acid in the presence of magnesium chloride catalyst and captured in sodium hydroxide absorber solution.

The absorber solution from the distillation is introduced into a flow injection analysis (FIA) system where it is acidified to form hydrogen cyanide (HCN). The hydrogen cyanide gas diffuses from the acid stream through a hydrophobic gas diffusion membrane into an alkaline acceptor stream. A sulfide complex reagent removes up to 50-mg/L sulfide automatically. The diffused cyanide passes through an amperometric flow cell. In the presence of cyanide, silver in the working electrode of the flow cell is oxidized at the

applied potential. The anodic current measured is directly proportional to the concentration of cyanide.

ASTM D7511-09 Standard Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection

This is a new standard test method that was developed by ASTM Committee D19 on Water to determine the concentration of total cyanide in drinking and surface waters, domestic wastewater, and industrial wastewater. Cyanide ion (CN-), hydrogen cyanide in water (HCN(aq)), and complexes of zinc, copper, cadmium, mercury, nickel, silver, and iron may be determined by this method. Cyanide ions from Au (I), Co (III), Pd (II), and Ru (II) complexes are only partially determined. The applicable range is method is 3 - 500 µg/L cyanide. The range can be extended to analyze higher concentrations by sample dilution or changing the sample loop volume.

ASTM D7511-09 decomposes complex cyanides by narrow band, low watt UV irradiation in a continuously flowing acidic stream at room temperature. Reducing and complexing reagents, combined with the room temperature narrow band low watt UV minimize interferences. The hydrogen cyanide generated passes through a hydrophobic membrane into a basic carrier stream. The cyanide concentration is determined by amperometry.

This method operates similarly to available cyanide methods OIA1677 and ASTM D6884-09. The available cyanide methods employ a preliminary ligand addition to liberate cyanide ion from weak to moderate metal cyanide complexes. These available cyanide methods were developed because they overcome significant interferences caused by the preliminary chlorination and/or distillation processes. Instead of ligands, ASTM D7511-09 irradiates the sample causing strong metal cyanide complexes plus all complexes measured by the available cyanide methods to liberate cyanide and generate hydrogen cyanide. Once the sample solution passes from the UV irradiation the measurement principle is equivalent to OIA1677 and/or ASTM D6888-09.

ASTM D7365-09a Standard Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide

ASTM Committee D19 on Water recently developed this practice. The practice is applicable for the collection and preservation of water samples for the analysis of cyanide. This practice addresses the mitigation of known interferences prior to the analysis of cyanide. Responsibilities of field sampling personnel and the laboratory are indicated. The sampling, preservation and mitigation of interference procedures described in this practice are recommended for the analysis of total cyanide, available cyanide, weak acid dissociable cyanide, and free cyanide by Test Methods D2036, D4282, D4374, D6888, D6994, D7237, D7284, and D7511. The information supplied in this practice can also be applied to other analytical methods for cyanide, for example, EPA Method 335.4.

Samples are collected in appropriate containers and mitigated for known interferences either in the field during sample collection or in the laboratory prior to analysis. Several topics are addressed in this standard including sample containers, preservation issues, holding time requirements, as well as procedures to mitigate potential interferences such as sulfur, sulfide, aldehydes, oxidizers, sulfite, thiosulfate, thiocyanate, particulates, carbonates, and nitrate/nitrite. The standard was developed after extensive collaboration at ASTM Committee D19 on Water and through an EPA/ASTM D19 workshop that was held on the topic in Denver, June 2008.