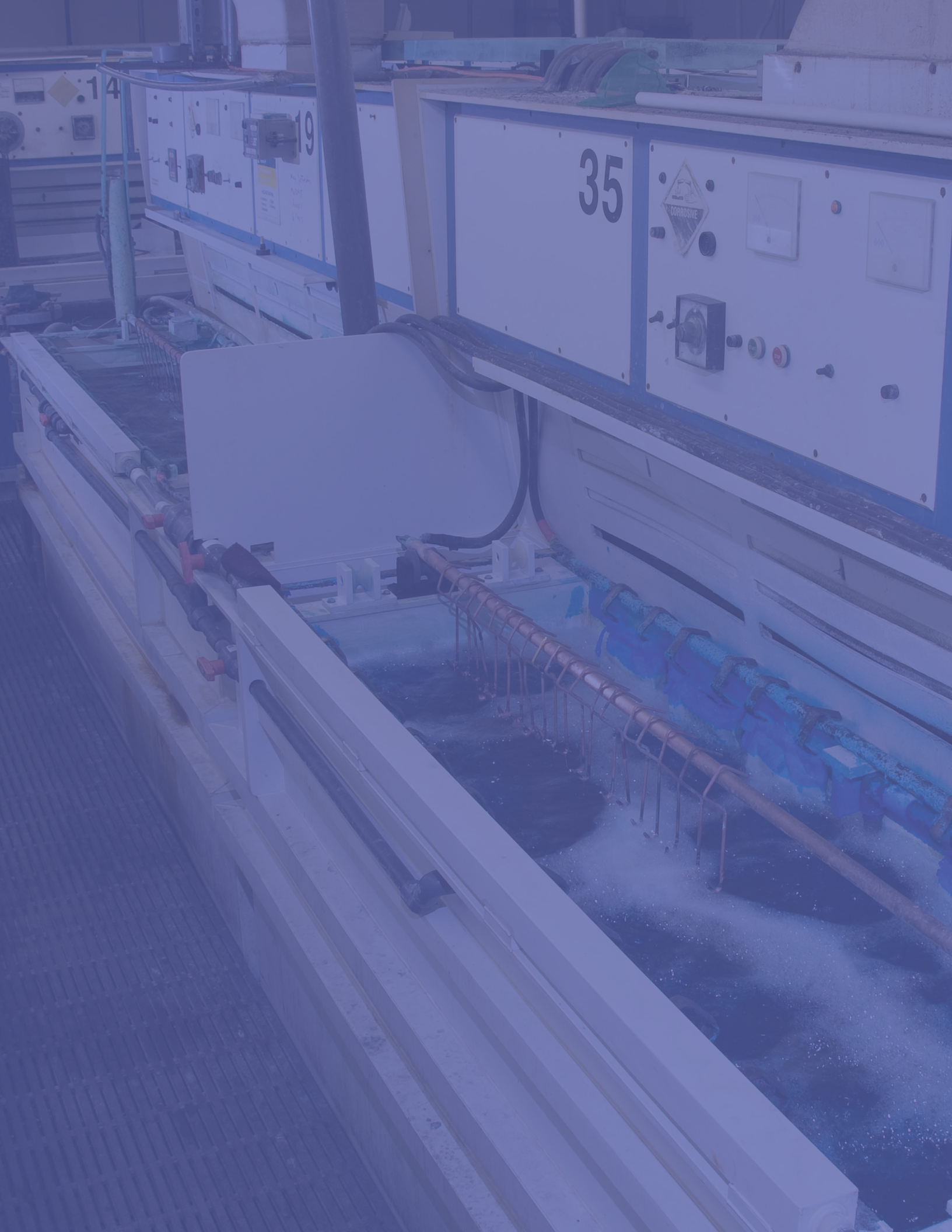




Cyanide Analysis Guide



Cyanide Toxicity



OI Analytical has been the leader in cyanide analysis instrumentation since 1990. Research supported by OI has made significant contributions to the science of cyanide analysis and the reliability of cyanide testing methods.

In this third edition of the Cyanide Analysis Guide we provide updated information on collecting and preserving samples, analytical interferences, and new ASTM and USEPA analytical methods.



Cyanide (CN^-) is a highly poisonous ion that binds with the enzyme cytochrome C oxidase. This complex inhibits cellular respiration and energy production, resulting in cytotoxic hypoxia affecting the central nervous system (CNS) and heart. Death typically occurs from respiratory arrest following CNS failure.^{1, 2, 3}



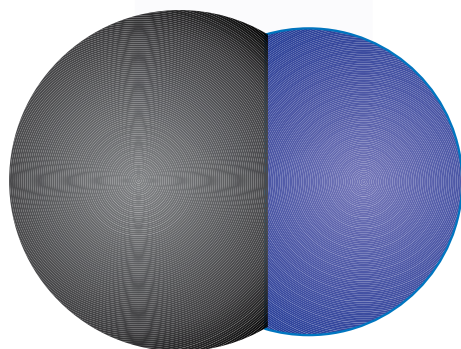
Cyanide compounds are used in a wide range of industrial applications. Hydrogen cyanide is used in the production of nylon 6/6 and methyl methacrylate plastics. Potassium or sodium cyanide are used in mining operations to leach gold from ore. Cyanide salts are used in metal plating baths for electroplating of brass, bronze, cadmium, copper, gold, silver and zinc.

Other industrial processes employing cyanide include; petroleum refining, steel production, microelectronics manufacturing, specialty chemical and pharmaceutical production.

The acute toxicity and wide spread industrial usage of cyanide makes environmental testing critically important. Intentional contamination of drinking water or food products with cyanide is also a potential Homeland Security threat.

Cyanide Analysis Chemistry

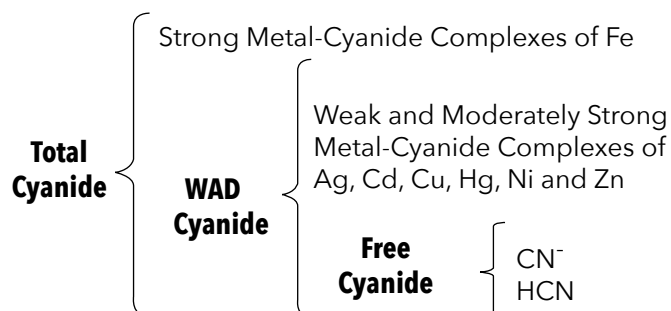
Cyanide refers to a monovalent anion consisting of carbon and nitrogen atoms with triple covalent bonds.



Cyanide is very reactive and readily forms metal-cyanide complexes and organic compounds.

The chemical composition of cyanide in environmental samples is affected by factors such as pH, temperature, trace metal content, and the presence of sulfur or sulfur compounds. A multitude of cyanide species of varying stability may be present in a sample. For these reasons cyanide testing can be a challenging analytical task.

Methods for the determination of cyanide are defined by the relative strength of metal complexes. From an analytical perspective cyanide compounds are broadly classified into three categories; total cyanide, available or weak acid dissociable (WAD) cyanide, and free cyanide.



Transition metals form strong bonds with the carbon atom of cyanide. Alkali metals form ionic bonds with the CN molecule. The relative stability of metal-cyanide compounds and complexes in water (listed in order of increasing stability) is presented below.

Cyanide Species

1. Free Cyanide CN^- , HCN
2. Simple Cyanide Compounds
 - a) Readily Soluble NaCN , KCN , $\text{Ca}(\text{CN})_2$, $\text{Hg}(\text{CN})_2$
 - b) Relatively Insoluble $\text{Zn}(\text{CN})_2$, CuCN , $\text{Ni}(\text{CN})_2$, AgCN
3. Weak Metal-Cyanide $\text{Zn}(\text{CN})_4^{2-}$, $\text{Cd}(\text{CN})_3^-$, $\text{Cd}(\text{CN})_4^{2-}$
4. Moderately Strong Metal-Cyanide Complexes $\text{Cu}(\text{CN})_2^-$, $\text{Cu}(\text{CN})_3^{2-}$, $\text{Ni}(\text{CN})_4^{2-}$, $\text{Ag}(\text{CN})_2^-$
5. Strong Metal-Cyanide $\text{Fe}(\text{CN})_6^{2-}$, $\text{Fe}(\text{CN})_6^{4-}$, $\text{Co}(\text{CN})_6^{4-}$, $\text{Au}(\text{CN})_2^-$, $\text{Hg}(\text{CN})_4^{2-}$

Free Cyanide

Free cyanide refers to the sum of hydrogen cyanide (HCN) and cyanide ion (CN^-) in a sample. Free cyanide is bioavailable and toxic to organisms in aquatic environments. At a pH of 7 or less free cyanide consists entirely of HCN.⁴ For analytical purposes free cyanide is defined as the amount of HCN liberated from a solution at pH 6.0.

Weak Acid Dissociable (WAD) Cyanide

WAD cyanide refers to metal cyanide complexes (Zn, Cd, Cu, Hg, Ni, and Ag) that dissociate under weak acid conditions of pH 4.5 to 6.

Cyanide Amenable to Chlorination (CATC)

CATC refers to cyanide complexes that dissociate and oxidize when exposed to chlorine under alkaline conditions.⁴ CATC consists of free cyanide and weak acid dissociable cyanide complexes. Testing for CATC is intended to measure the effectiveness of cyanide destruction by chlorination. To determine CATC a sample is split into two portions, with one portion tested for total cyanide and the second portion treated with calcium hypochlorite (to destroy cyanide) prior to a total cyanide test. The difference in total cyanide contents constitutes CATC cyanide.

Available Cyanide

Available cyanide encompasses free cyanide and WAD cyanide complexes which dissociate under mildly acidic conditions of pH 3 to 6. Available cyanide is determined by ligand exchange pretreatment followed by flow injection analysis of the liberated CN^- .⁴

Total Cyanide

Total Cyanide refers to the sum of all cyanide-containing compounds in a sample, including free cyanide, WAD cyanide compounds and strong metal-cyanide complexes. Strong acidic conditions ($\text{pH} < 2$) are required to dissociate strong metal-cyanide complexes and release free cyanide. Analytical methods for total cyanide determination employ an acid distillation or UV irradiation step to release free cyanide.⁴

Interferences

There are a number of known interferences associated with cyanide methods that employ an acid distillation step. In fact, the USEPA Solutions to Analytical Chemistry Problems with Clean Water Act Methods⁵ ("Pumpkin Guide") notes; "Next to oil and grease, cyanide is the pollutant for which the most matrix interferences have been reported to EPA." For accurate results it is important to select an analytical technique and method that are free of these interferences.

Sulfide - Sulfide when present in samples can cause low or high cyanide recoveries. Low recoveries are caused by sulfide reacting with cyanide to form thiocyanate. High recoveries occur when volatilized sulfide distills over and reacts with colorimetric reagents and is erroneously detected as cyanide.

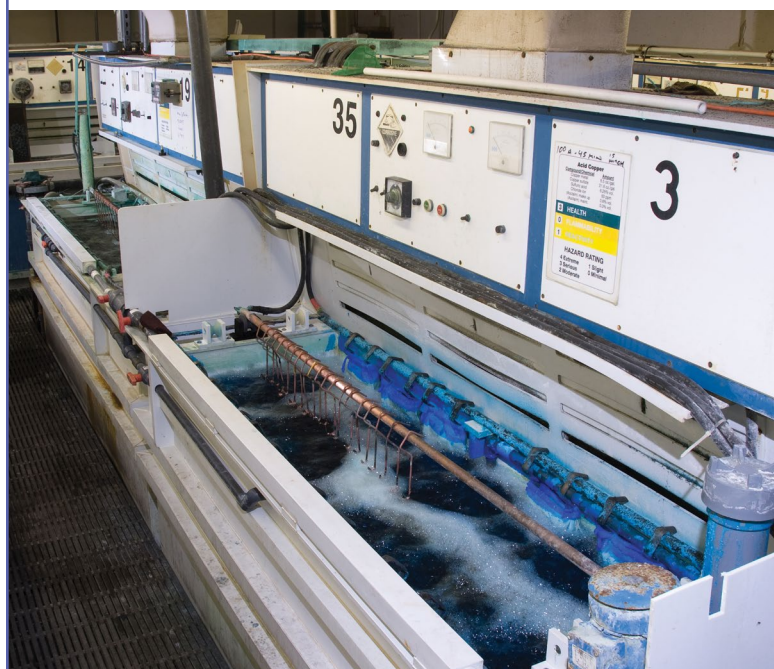
Thiocyanate - Distillation of samples containing thiocyanate (SCN^-) can result in low cyanide recoveries. Thiocyanate decomposes to oxidized sulfur compounds during distillation, which react with cyanide in the absorber solution and cause a negative bias.

Thiosulfate - Samples containing thiosulfate ($\text{S}_2\text{O}_3^{2-}$) salts can react during acid distillation to form cyanate compounds and cause a negative bias.

Nitrate and Nitrite - Samples containing nitrate and/or nitrite and organic compounds can react during acid distillation to form cyanide and cause a positive bias.

Sulfite - Wastewater effluent samples that have been chlorinated and then de-chlorinated using sulfur dioxide will contain sulfites. Acidification of sulfite during distillation forms H_2SO_3 , which decomposes to form SO_2 gas. This SO_2 gas is absorbed in the NaOH scrubber solution, (along with HCN gas), forming Na_2SO_3 . Because a stream of air continuously passes through the NaOH scrubber, the absorbing solution contains sulfite (SO_3^{2-}), dissolved O_2 and CN^- . The sulfite and oxygen will oxidize CN^- forming cyanate (OCN^-) resulting in a negative interference.

Oxidizing Agents - Chlorine, hypochlorite and other oxidizing agents will decompose most cyanides. If oxidizing agents are present during acid distillation they will react with cyanide and cause a negative bias. In cases where chlorine or another oxidant is known to be present, addition of a reducing agent such as ascorbic acid, sodium arsenite (NaAsO_2), or sodium borohydride (NaBH_4) is recommended in some methods. Careful testing for cyanide recovery is necessary to avoid secondary reactions between the reducing agent and other substances that may be present in a sample.





Cyanide Analysis Methods

An extensive list of cyanide analysis methods have been issued by the United States Environmental Protection Agency (USEPA), American Society for Testing and Materials (ASTM), International Standards Organization (ISO), and American Water Works Association (AWWA).

Aquatic Free Cyanide

ASTM Method D7237-10 ⁶

This method applies to free cyanide in aqueous wastewater and effluents. Free cyanide ions (HCN and CN⁻) and metal-cyanide complexes that dissociate into free cyanide at pH 6 to pH 8 in an aquatic environment are measured by this method using a FIA gas-diffusion technique with amperometric detection. This method is comparable to 4500-CN- R Free Cyanide by Flow Injection, Gas Diffusion, and Amperometric Measurement.

Available Cyanide

USEPA Method OIA-1677-09 ⁷ &

ASTM Method D6888-09 ⁸

These USEPA-approved methods are based upon a ligand-exchange, gas diffusion technique coupled with amperometric detection. The concentration of available cyanide in wastewater, effluents and drinking water may be determined by these methods. This method is comparable to 4500-CN- Q Weak and Dissociable Cyanide by Flow Injection, Gas Diffusion, and Amperometric Measurement.

Methods for International Cyanide Management Code

ASTM D7728-11 ⁹

This standard provides guidance on selection of analytical methods for implementation of the International Cyanide Management Code. Test methods in this guide cover the gold leaching process, environmental monitoring, protection of human health and aquatic wildlife.

Recovery of Aqueous Cyanides by Extraction from Mine Rock and Soil

ASTM D7572-11a ¹⁰

This standard provides guidance on the collection, extraction, and preservation of mine rock and soil samples for cyanide analysis of the extracts.

Standard Test Methods for Cyanides in Water

ASTM D2036-09 ¹¹

This standard covers test methods for determination of cyanides in water. Methods for total cyanide after distillation, cyanides amenable to chlorination (CATC), and weak acid dissociable (WAD) cyanides are included.

Standard Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide.

D7365-09a

This 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.

Total Cyanide

USEPA Method 335.4

This method employs acid distillation to break down strong metal cyanide complexes and release HCN gas, which is trapped in a scrubber solution. This solution is colorimetrically analyzed using chloramine-T and pyridine-barbituric acid reagents.

Total Cyanide

ASTM Method D7511-12 ¹²

This USEPA-approved method uses in-line UV digestion to break down strong metal cyanide complexes and release HCN gas, followed by gas diffusion separation and amperometric detection. ASTM D7511-12 can be used for analyzing wastewater samples for NPDES compliance reporting. This method is comparable to Standard Method 4500-CN-P Total Cyanide by Segmented Flow Injection, UV-Irradiation with Gas Diffusion, and Amperometric Measurement.

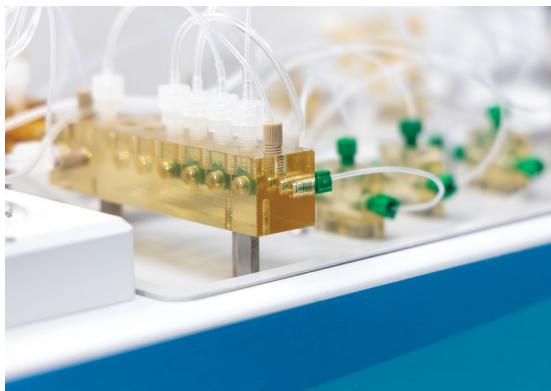
Total Cyanide

ISO-14403:2002 ¹³

This method is used to determine total cyanide in water samples using a colorimetric flow injection analysis technique. Amperometric detection is also allowed as an option in this method.

Available Cyanide

Learn about the products used in this analysis:



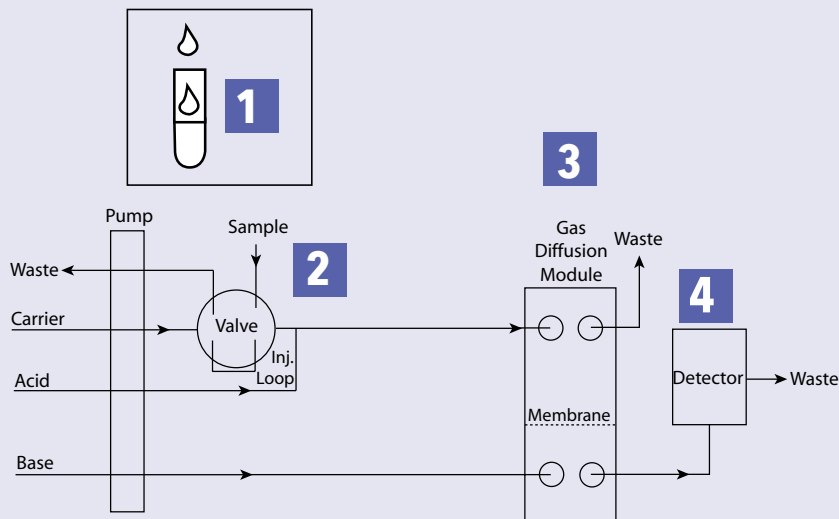
The FS3700 is a compact, modular system for flow injection analysis of available or total cyanide.

The FS3700 measures available cyanide by a ligand-exchange, gas diffusion technique coupled with amperometric detection in accordance with USEPA Method OIA-1677-09 and ASTM D6888-09. This non-distillation technique provides accurate measurement of available cyanide in the presence of thiocyanate, sulfite and thiosulfate interferences.

A sulfide removal acidification reagent is added in-line to samples containing this interference. A schematic drawing of the FS3700 highlighting the principal steps of the ligand-exchange, gas diffusion cyanide analysis technique is presented below.

Principle of Operation

For available cyanide measurement, samples are treated with ligand exchange reagents to liberate the cyanide ion (CN^-) (1). A sample is then injected into a carrier stream and acidified (2). Under acidic conditions CN^- converts to hydrogen cyanide (HCN) and diffuses across a hydrophobic membrane into a basic acceptor solution (3), where it converts back to CN^- and is carried into the flow cell of an amperometric detector. Cyanide ions react with a silver electrode and generate current proportional to the cyanide ion concentration (4). WinFlow software displays the detector response in real-time as a peak as the sample passes through the flow cell. The resulting peak height is proportional to cyanide concentration present in the sample.



1 Ligand exchange Pretreatment
 $\text{MCN}^- + \text{LE} \rightarrow \text{MLE} + \text{CN}^-$

2 Acidification
 $\text{CN}^- + \text{H}^+ \rightarrow \text{HCN (g)}$

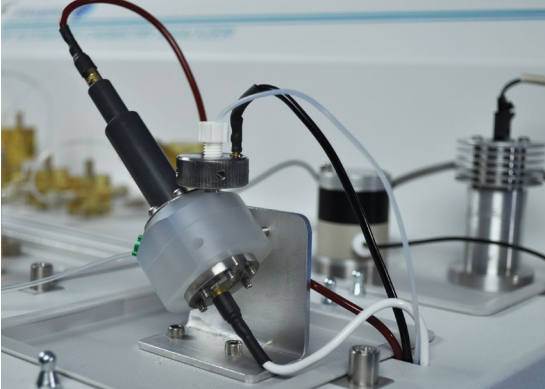
3

 $\text{HCN} \rightarrow \text{CN}^-$ (in basic acceptor solution)

4 Amperometric Detection
 $2 \text{CN}^- + \text{Ag} \rightarrow \text{Ag}(\text{CN})_2^- + \text{e}^-$ at +0.0 V

Total Cyanide

Learn about the products used in this analysis:



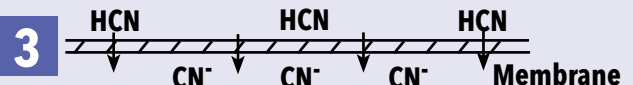
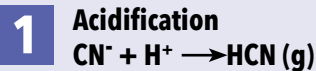
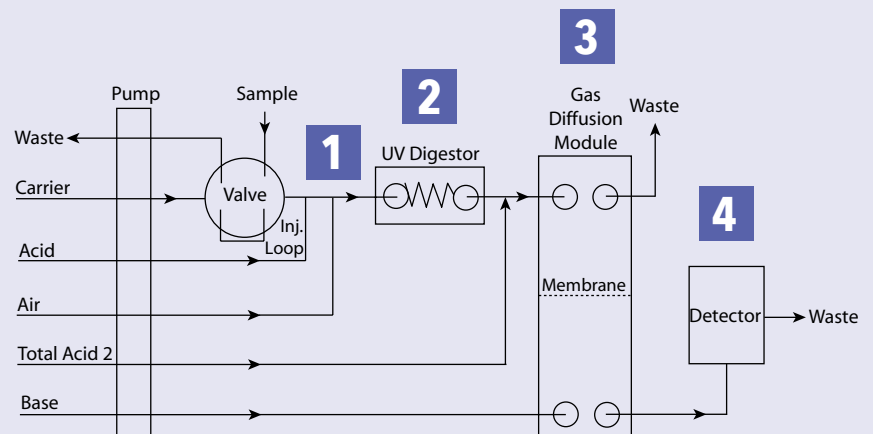
The FS3700 measures total cyanide by a UV digestion, gas diffusion technique coupled with amperometric detection in accordance with ASTM Method D7511-12.

This non-distillation technique is particularly effective for applications where thiocyanate is present to avoid cyanide loss or positive interference. ASTM D7511-12 is USEPA-approved for analysis of wastewater samples for NPDES compliance reporting.

A schematic drawing of the FS3700 highlighting the principal steps of the UV digestion, gas diffusion cyanide analysis technique is presented below.

Principle of Operation

For total cyanide measurement, a sample is injected into a carrier stream, segmented and acidified. Under acidic conditions the weak acid dissociable cyanide complexes convert to HCN (1) and the strong metal-cyanide complexes are exposed to ultraviolet light in the UV digestion module (2) where they break down and release HCN. The HCN gas from all cyanide species present in the sample diffuses across a hydrophobic membrane into a basic acceptor solution (3), where it converts back to CN^- and is carried into the flow cell of an amperometric detector. Cyanide ions react with a silver electrode and generate current proportional to the cyanide ion concentration (4). WinFlow software displays the detector response in real-time as a peak as the sample passes through the flow cell. The resulting peak height is proportional to cyanide concentration present in the sample.



Total Cyanide - USEPA Method 335.4

Learn about the products used in this analysis:

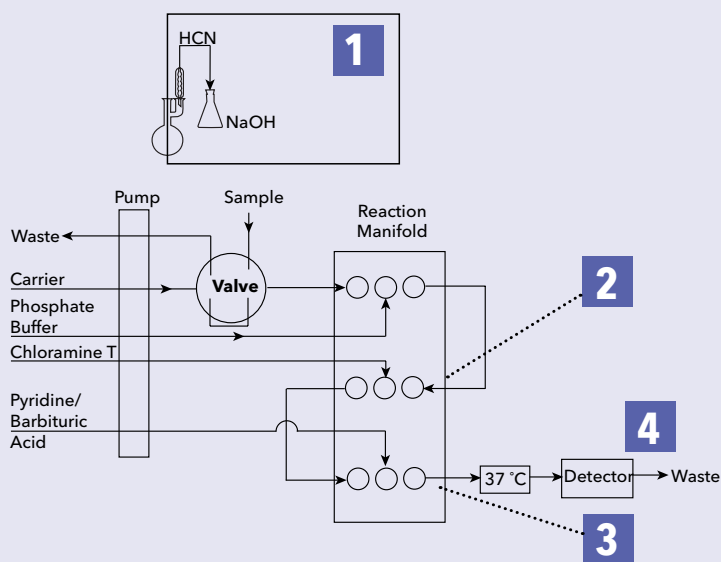


The FS3700 also measures total cyanide in post-distillation samples by a colorimetric reaction involving chloramine-T and pyridine/barbituric acid reagents, followed by spectrophotometric measurement at 570 nm.

The USEPA notes a potential drawback of method 335.4 in their publication; Solutions to Analytical Chemistry Problems with Clean Water Act Methods stating; "If sulfite and thiosulfate are present there is no way to accurately determine cyanide if heat is applied. In these situations a non-distillation method such as D6888-04, or method OIA-1677 may be used." A schematic drawing of the FS3700 configured to perform USEPA Method 335.4 is presented below.

Principle of Operation

Samples to be analyzed must undergo a preliminary 2 hour sulfuric acid distillation step to breakdown cyanide complexes and release HCN gas, which is trapped in a sodium hydroxide scrubber solution (1). This NaOH solution is injected into a carrier stream and reacted with chloramine-T (2), converting the cyanide ion to cyanogen chloride. A pyridine and barbituric acid reagent is then reacted with cyanogen chloride (3) producing a red-colored complex which passes through a 37 °C heater and into the flow cell of a photometric detector for measurement at 570 nm (4). WinFlow software displays the detector response in real-time as a peak. The resulting peak height is proportional to the cyanide concentration present in the sample.



1 2 Hour Sulfuric Acid Distillation
 $\text{MCN}^- + \text{H}_2\text{SO}_4 \rightarrow \text{HCN (g) in NaOH}$

2 $\text{HCN} + \text{NH}_2\text{Cl} \rightarrow \text{NCCI}$

3 $\text{NCCI} + \text{C}_5\text{H}_5\text{N} / \text{C}_4\text{H}_4\text{O}_3\text{N}_2 \rightarrow (\text{red-colored complex})$

4 Photometric Detection at 570 nm

Reference & Links

Publications and website links referenced within this guide along with additional sources of information on cyanide analysis are detailed below.

References

¹ Draft Toxicological Profile for Cyanide, U.S. Dept. of Health and Human Services, Agency for Toxic Substances and Disease Registry, September, 2004.

² Cyanide Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review, R. Eisler, U.S. Fish and Wildlife Service, Biological Report 85(1.23), December, 1991.

³ Public Health Goal for Cyanide in Drinking Water, California Environmental Protection Agency, Pesticide and Environmental Toxicology Section, December, 1997.

⁴ D 6696-05 Standard Guide for Understanding Cyanide Species, ASTM International, 2005

⁵ Solutions to Analytical Chemistry Problems with Clean Water Act Methods, USEPA Office of Science and Technology, March 2007.

⁶ D 7237-10 Standard Test Method for Aquatic Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection, ASTM International.

⁷ Method OIA-1677-09 Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry, EPA-821-R-99-013; U.S. Environmental Protection Agency, August 1999.

⁸ D 6888-09 Standard Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection, ASTM International

⁹ D 7728-11 Standard Guide for Selection of ASTM Analytical Methods for Implementation of International Cyanide Management Code Guidance, ASTM International.

¹⁰ D 7572-11a Standard Guide for Recovery of Aqueous Cyanides by Extraction from Mine Rock and Soil, ASTM International.

¹¹ D 2036-09 Standard Test Methods for Cyanides in Water, ASTM International.

¹² D7511 Standard Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection (astm.org)

¹³ ISO-14403:2002 Water quality- Determination of total cyanide and free cyanide by continuous flow analysis, International Organization for Standardization.

¹⁴ D 7284-08 New Standard Test Method for Total Cyanide in Water by Midi or Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection, ASTM International.

Links

American Society of Testing & Materials;
www.astm.org

Cyanide and Science;
www.cyantists.com

International Cyanide Management Code;
www.cyanidecode.org

National Mining Association;
www.nma.org

International Organization for Standardization (ISO); www.iso.org

National Environmental Methods Index;
www.nemi.gov

USEPA Clean Water Act Methods "Pumpkin Book"; www.epa.gov/waterscience/methods

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- 1) The tissue in plants that brings water upward from the roots;
- 2) a leading global water technology company.

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OI Analytical, a Xylem brand
1725 Brannum Lane
Yellow Springs, OH 45387
 +1.937.767.7241
 xylem-lab@xylem.com
 YSI.com

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