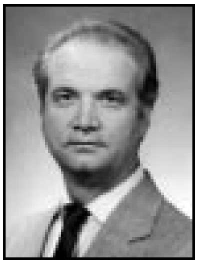

Advice & Counsel

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Available Cyanide

Dear Advice & Counsel,
I have been following your periodic articles on the issue of cyanide analytical problems over the years, and now wonder if some of your concerns about the analysis of cyanide have been addressed by the U.S. EPA, in their recently proposed procedure for "Available Cyanide." Will this new procedure solve the metal finishing industry's problems with cyanide analysis?

Signed, I ♥ Cyanide

Dear ♥,
I've seen you wearing that huge button!

I suppose we all will have to add another type of cyanide to our current lexicon. In addition to Total, Free, Amenable, Weak Acid Dissociable (WAD), we now introduce you to "Available." Let's dip into the EPA Internet site, and bring everybody up to speed:

Available Cyanide by Flow Injection/Ligand Exchange (Method OIA-1677)

Summary

The U.S. Environmental Protection Agency (EPA) has proposed in the *Federal Register* a method that will improve EPA's capability to accurately measure available cyanide in wastewater through use of a ligand exchange/flow injection/amperometric technique. This method is being proposed for approval for use in wastewater at 40 CFR part 136.

Background

The EPA publishes laboratory analytical methods that are used by industrial and municipal facilities in analyzing the chemical and biological components of wastewater, drinking water and sediment. This type of environmental sampling is required by EPA regulations under the authority of the Clean Water Act and the Safe Drinking Water Act.

Method 0IA- 1677 was developed by ALPKEM, a Division of 0I Analytical, in cooperation with the University of Nevada Reno Mackay School of Mines, as a way to measure available cyanide without the interference problems of the currently approved available cyanide methods.

EPA is proposing Method 0IA-1677 as another testing procedure for compliance monitoring under the National Pollutant Discharge Elimination System; ambient water quality monitoring; development of effluent limitations guidelines; and general laboratory use. This rulemaking does not propose to repeal any of the currently approved methods that test for available cyanide. Each permitting authority must decide which method is appropriate for its needs.

This proposal would amend the Guidelines Establishing Test Procedures for the Analysis of Pollutants under section 304(h) of the Clean Water Act to augment currently approved available cyanide test procedures with EPA Method 0IA-1677: Available Cyanide by Flow Injection with Ligand Exchange.

Benefits of Method OIA-1677

- Elimination of potential interferences
- Lower detection limit
- Better accuracy and precision
- Improved laboratory safety
- Lower costs of environmental measurements through a rapid automated process
- Reduction of hazardous chemical use and associated waste generation

The Method

Method 0IA-1677 provides another procedure for available cyanide. Samples are treated with a ligand exchange solution to liberate available cyanide, which is then introduced into an automated flow-injection analysis system for measurement of the liberated cyanides.

Method 0IA-1677 contains QC acceptance criteria for all standardized QC tests. Compliance with these criteria will allow the data user to evaluate the quality of the results. This requirement increases the reliability of results and provides a means to monitor analytical performance, thereby providing a basis for sound, defensible data.

Additional Information & Copies

For additional information concerning this action, contact Dr. Maria Gomez-Taylor at the U.S. Environmental Protection Agency, Office of Water, Engineering and Analysis Division (4303), 401 M Street, S.W., Washington, D.C.; at 202/260-1639; e-mail: Gomez-Taylor.Maria@epamail.epa.gov.

The Federal Register notice contains instructions on how to obtain additional information and how to review the public record on this rulemaking. You also may obtain copies of Method 0IA-1677 through the EPA National Center for Environmental Publications and Information (NCEPI), 11029 Kenwood Road, Cincinnati, OH 45242.

1.0 Scope and Application

1.1—This method is for determination of available cyanide in water and wastewater by flow injection, ligand exchange, and amperometric titration. The method is for use in EPA's data-gathering and monitoring programs associated with the Clean Water Act, Resource Conservation and Recovery Act, Comprehensive Environmental Response, Compensation and Liability Act and Safe Drinking Water Act.

1.2—Cyanide ion (CN), hydrogen cyanide in water (HCN_{aq}), and the cyano-complexes of zinc, copper, cadmium, mercury, nickel and silver may be determined by this method.

1.3—The presence of polysulfides and colloidal material may prove intractable for application of this method.

1.4—The method detection limit (MDL) is 0.5 µg/L (ppb) and the minimum level (ML) is 2.0 µg/L (ppb). The dynamic range is approximately 2.0 µg/L (ppb) to 5.0 mg/L (ppm) cyanide ion using a 200 L sample loop volume. Higher concentrations can be determined by dilution of the original sample or by reducing volume of the sample loop.

1.5—This method is used by analysts experienced with flow injection equipment or under close supervision of such qualified persons.

1.6—This method is “performance-based.” The laboratory is permitted to modify the method to overcome interferences or to lower the cost of measurements, provided that all performance criteria in this method are met.

2.0 Summary of Method

2.1—The analytical procedure employed for determination of available cyanide is divided into two parts: Sample pretreatment and cyanide detection. In the pretreatment step, ligand-exchange reagents are added at room temperature to 100 mL of a cyanide-containing sample. The ligand-exchange reagents form thermodynamically stable complexes with the transition metal ions listed in Section 1.2, resulting in the release of cyanide ion from the metal-cyano complexes.

Cyanide detection is accomplished using a flow-injection analysis (FIA) system (Reference 15.6). A 200-µL (author’s note: The procedure actually indicates 200 liters, but I think that is a typo) aliquot of the pretreated sample is injected into the flow injection manifold of the system. The addition of hydrochloric acid converts cyanide ion to hydrogen cyanide (HCN) that passes under a gas diffusion membrane. The HCN diffuses through the membrane into an alkaline receiving solution where it is converted back to cyanide ion. The cyanide ion is monitored amperometrically with a silver working electrode, silver/silver chloride reference electrode, and platinum/stainless steel counter-electrode at an applied potential of zero volt. The current generated is proportional to the cyanide concentration present in the original sample. Total analysis time is approximately two minutes.

2.2—The quality of the analysis is assured through reproducible calibration and testing of the FIA system.

Interferences

Interferences extracted from samples will vary considerably from source to source, depending upon the diversity of the site being sampled.

Sulfide

Sulfide is a positive interferent in this method (Ref. 15.3 and 15.4), because an acidified sample containing sulfide liberates hydrogen sulfide that is passed through the membrane and produces a signal at the silver electrode. In addition, sulfide ion reacts with cyanide ion in solution to reduce its concentration over time. To overcome this interference, the sulfide ion must be precipitated with lead ion immediately upon sample collection. Sulfide ion and lead sulfide react with cyanide ion to form thiocyanate, which is not detected in the analytical system. Tests have shown that if lead carbonate is used for sulfide precipitation, the supernate containing cyanide must be filtered immediately to avoid loss of cyanide through reaction with precipitated lead sulfide.

Water-soluble Aldehydes

Water-soluble aldehydes react with cyanide to form cyanohydrins that are not detected by the analytical system.

Hypochlorite & Sulfite

Hypochlorite and sulfite oxidize cyanide to non-volatile forms. Procedures for the removal of these substances are provided in Sections 8.2.2 and 8.2-3.

The presence of colloids cause rapid cyanide losses. Filtration can be used to remove colloids, but may have an adverse affect on measured cyanide levels. This method should not be applied to samples with large amounts of colloids, unless the laboratory is able to demonstrate that cyanide concentration measurements in a sample are not affected by filtration.

Based on the above information, it would appear to me that this new analytical procedure has no applicability to monitoring of metal finishing discharges, which are regulated for either Total Cyanide, Amenable Cyanide, or both. Because this procedure detects cyanides complexed with non-amenable nickel ions, but not cyanides complexed with iron, it basically could be expected to yield a cyanide value somewhere between the total and the amenable values. Because metal finishing wastewaters do typically contain sulfides and colloids, I would expect the new procedure to be fraught with the same perplexing problems the existing procedures have. EPA indicated concurrence by their statement in paragraph 1.3 above.

The EPA is to be commended for recognizing and working on the analytical problem, but this appears to be a case of “close, but no cigar.” P&SF