ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 136

[FRL–6121–5]

RIN 2040–AC76

Guidelines Establishing Test Procedures for the Analysis of Pollutants; Available Cyanide

AGENCY: Environmental Protection Agency (EPA).

ACTION: Proposed rule.

SUMMARY: This proposed regulation would amend the Guidelines Establishing Test Procedures for the Analysis of Pollutants under Section 304(h) of the Clean Water Act by adding Method OIA–1677: Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry. Method OIA–1677 employs flow injection analysis (FIA) to measure ''available cyanide.'' Method OIA–1677 is being proposed as an additional test procedure for measuring the same cyanide species as are measured by currently approved methods for cyanide amenable to chlorination (CATC). In some matrices, CATC methods are subject to significant test interferences. In contrast, Method OIA–1677 demonstrates greater specificity for cyanide for matrices in which interferences have been encountered using CATC methods. In addition, Method OIA–1677 measures cyanide at lower concentrations and offers improved precision and accuracy over currently approved CATC methods. Method OIA–1677 also offers improved laboratory safety and reduces laboratory waste compared to currently approved CATC methods. This significantly reduces the generation of hazardous waste by the laboratory. Cyanide analysis by Method OIA–1677 is also more rapid than by currently approved methods.

DATES: Comments on this proposal must be submitted on or before September 8, 1998.

ADDRESSES: Send written comments on the proposed rule to ''Method OIA–1677'' Comment Clerk (Docket #W–98–08); Water Docket (4101); Environmental Protection Agency; 401 M Street, SW., Washington, DC 20460. Commenters are requested to submit any references cited in their comments. Commenters are also requested to submit an original and 3 copies of their written comments and enclosures. Commenters that want receipt of their comments acknowledged should include a self addressed, stamped envelope. All comments must be postmarked or delivered by hand. No facsimiles (faxes) will be accepted.

Data available: A copy of the supporting documents cited in this proposal is available for review at EPA's Water Docket; 401 M Street, SW, East Tower Basement, Washington, DC 20460. For access to docket materials, call (202) 260–3027 between 9 a.m. and 3:30 p.m. for an appointment. An electronic version of Method OIA–1677 will be available via the Internet at http://www.epa.gov/OST/Tools.

FOR FURTHER INFORMATION CONTACT: Dr. Maria Gomez-Taylor, Engineering and Analysis Division (4303), USEPA Office of Science and Technology, 401 M Street, SW, Washington, DC 20460, or call (202) 260–1639.

SUPPLEMENTARY INFORMATION:

Potentially Affected Entities

EPA Regions, as well as States, Territories and Tribes authorized to implement the National Pollutant Discharge Elimination System (NPDES) program, issue permits that comply with the technology-based and water quality-based requirements of the Clean Water Act. In doing so, the NPDES permitting authority, including authorized States, Territories, and Tribes, make a number of discretionary choices associated with permit writing, including the selection of pollutants to be measured and, in many cases, limited in permits. If EPA has ''approved'' standardized testing procedures (i.e., promulgated through rulemaking) for a given pollutant, the NPDES permit must include one of the approved testing procedures or an approved alternate test procedure. Therefore, entities with NPDES permits could be affected by the standardization of testing procedures in this rulemaking. These entities may be affected because NPDES permits may incorporate one of the standardized testing procedures in today's rulemaking. In addition, when a State, Territory, or authorized Tribe provides certification of federal licenses under Clean Water Act section 401, States, Territories and Tribes are directed to use the standardized testing procedures. Categories and entities that may ultimately be affected include:

Category	Examples of potentially affected entities
State and Territorial Governments and Indian Tribes	States, Territories, and Tribes authorized to administer the NPDES permitting program; States, Territories, and Tribes providing certification under Clean Water Act section 401; Governmental NPDES permittees.
Industry	Industrial NPDES permittees.
Municipalities	Publicly-owned treatment works with NPDES permits.

This table is not intended to be exhaustive, but rather provides a guide for readers regarding entities likely to be affected by this action. This table lists the types of entities that EPA is now aware could potentially be affected by this action. Other types of entities not listed in the table could also be affected. If you have questions regarding the applicability of this action to a particular entity, consult the person listed in the preceding **FOR FURTHER INFORMATION CONTACT** section.

I. Authority

Today's proposal is pursuant to the authority of sections 301, 304(h), and 501(a) of the Clean Water Act (CWA), 33 U.S.C. 1314(h), 1361(a) (the ''Act''). Section 301 of the Act prohibits the discharge of any pollutant into navigable waters unless the discharge complies with a National Pollutant Discharge Elimination System (NPDES) permit, issued under section 402 of the Act. Section 304(h) of the Act requires the Administrator of the EPA to ''promulgate guidelines establishing test procedures for the analysis of pollutants that shall include the factors which must be provided in any certification pursuant to section 401 of this Act or permit applications pursuant to section 402 of this Act.'' Section 501(a) of the Act authorizes the Administrator to ''prescribe such regulations as are necessary to carry out his function under this Act.'' The Administrator also has made these test procedures applicable to monitoring and reporting of NPDES permits (40 CFR part 122, § 122.21, 122.41, 122.44, and 123.25), and implementation of the pretreatment standards issued under section 307 of the Act (40 CFR part 403, §§ 403.10 and 402.12).

II. Background

A. Cyanide

Cyanides are, as a class, one of the toxic pollutants pursuant to section 307(a)(1) of CWA (see the list of toxic pollutants at 40 CFR 401.15). Total cyanide is a priority pollutant as derived from the toxic pollutant list (see 40 CFR Part 423, Appendix A).

In the context of analytical methods, cyanide or cyanides refers to the group of simple and complex chemical compounds that can be determined as cyanide ion (CN^-). Cyanides are of the form $A(CN)_X$, where A is an alkali such as sodium or potassium, or a metal such as calcium, and x is the number of CN groups attached to A. Cyanides are present in aqueous solutions as CN^- and as hydrocyanic acid (HCN or hydrogen cyanide). The proportion of CN^- and HCN in solution is dependent on the pH and the dissociation constant for HCN. At low pH, the cyanide exits as HCN; at high pH, it exists as CN^-. At the near-neutral or slightly acidic pH of most natural waters, nearly all cyanide is present as HCN. Most of the metal cyanides are insoluble or only slightly soluble in water but may form a variety of soluble cyanide complexes when a cyanide such as potassium or sodium cyanide is present.

Hydrogen cyanide is the cyanide species most toxic to aquatic life. The toxicity of the other cyanides is attributable to the degree of their dissociation and conversion to HCN. Some cyano-metal complexes, such as those of zinc and cadmium, dissociate almost totally (i.e., a knowledge of the complex can be used to determine the amount of cyanide). Other cyano-metal complexes, such as those of iron, dissociate little. For these complexes, a large amount can be present without cyanide being detected. Still, other complexes, such as mercury, nickel, and silver, dissociate partially and only under certain conditions. For complexes that release some, but not all, of the cyanide ion, the amount of dissociation must be known to determine the amount of cyanide. This total, partial, or near lack of dissociation presents a difficulty in the determination of cyanides, as explained below.

B. Need for Improved Methods for Cyanide

Methods proposed in Guidelines Establishing Test Procedures for the Analysis of Pollutants under section 304(h) of the Clean Water Act are listed at Title 40 of the Code of Federal Regulations, § 136.3. EPA had received numerous letters and comments regarding interference problems when the currently approved methods were used to test certain sample matrices and was therefore aware of the need for a cyanide method that reduced or eliminated these interferences. A method for measuring available cyanide by flow injection analysis (FIA) had been developed by ALPKEM in cooperation with the University of Nevada at Reno, Mackay School of Mines in 1995. Besides overcoming most matrix effect problems, Method OIA–1677 uses amperometry as an innovative technology to improve the detection of available cyanide. Method OIA–1677 is faster, more accurate and precise, and allows determination of available cyanide at lower concentrations than currently approved methods. Method OIA–1677 is also safer because it requires a smaller amount of a potentially hazardous sample, requires less manual operations where accidents could lead to exposure, and uses less hazardous substances in the sample preparation and determinative steps.

C. Methods for Determination of Cyanide

Methods presently approved at 40 CFR Part 136 measure cyanide in two ways: as ''total cyanide'' and ''cyanide amenable to chlorination'' (CATC). A third way is as ''weak-acid dissociable'' (WAD) cyanide but there is presently no approved method for WAD cyanide in 40 CFR Part 136. Methods for determination of total cyanide attempt to measure all cyanide species that may dissociate in the environment over time and when exposed to natural forces (e.g., heat, light, water of varying hardness, pH) but ultimately fail to do so because many species cannot be dissociated completely under normal laboratory conditions. The CATC and WAD methods, and Method OIA–1677, which employs ligand exchange, all attempt to measure ''available'' cyanide, i.e., cyanide species that dissociate in the presence of chlorine and/or acid. The species of cyanide measured by these methods are cyanide ion (CN^-), hydrogen cyanide (HCN), and the cyano-complexes of zinc, copper, cadmium, mercury, nickel, and silver. The net result is that the WAD, CATC, and OIA–1677 methods all measure nearly the same species of cyanide. The term ''available cyanide'' is used in Method OIA–1677 because the chlorination reaction used in the CATC methods is not employed, although the cyanides determined are the same.

Methods for total cyanide employ reflux distillation in the presence of sulfuric acid and magnesium chloride to dissociate CN_- from cyanide-metal complexes. This process is more vigorous than the dissociation processes used in the WAD, CATC, and ligand-exchange methods, and a greater number of cyanide species are dissociated in the distillation process. The HCN liberated during the distillation is captured in an aqueous solution of sodium hydroxide and the cyanide in the solution is determined spectrophotometrically or titrimetrically.

Cyanide amenable to chlorination (CATC) is determined by chlorinating the available cyanide in the sample using calcium hypochlorite ($Ca(OCl)_2$), measuring the HCN using the total procedure, and finding the CATC concentration by difference between the total cyanide measured before and after the chlorination.

Available cyanide is determined in Method OIA–1677 by flow injection, ligand exchange, and amperometric detection. The ligand-exchange reagents displace cyanide from cyano-metal complexes. Further details of Method OIA–1677 are given in a description of the method below.

As stated above, no method measures all species of cyanides because several species (such as cobalt and gold cyanides) are so stable that they are either not dissociated or are only slightly dissociated in the reflux distillation or chlorination processes. Method OIA–1677 and CATC methods measure easily dissociable and partially dissociable species. Most notable among the partially dissociable species are the certain cyanides of nickel, mercury, and silver when these cyanides are present at high concentrations (ca 2 mg/L). These cyanides are recovered in the range of 55—85 percent in the CATC methods. In contrast, these species are recovered completely in Method OIA–1677, and this is the significant difference between the performance of Method OIA–1677 and approved methods for CATC. As a result, if a sample contains high concentrations of certain cyanides of nickel, mercury, or silver, the result will be somewhat higher when Method OIA–1677 is used, provided no interferences are present. At concentrations below approximately 0.2 mg/L, the recoveries of these cyanides from CATC methods and Method OIA–1677 are all approximately equivalent and near 100 percent.

D. Effect of Interferences on Cyanide Methods

The CATC determination is highly susceptible to interferences, as many substances other than cyanides can react in the chlorination process. For an overview of the nature and magnitude of these interferences, see the paper

presented by Goldberg, et. al. at the Seventeenth Annual EPA Conference on Analysis of Pollutants in the Environment, May 3–5, 1994 (available from the EPA Sample Control Center, 300 N. Lee Street, Alexandria, VA 22314 (703–519–1140). Interferences in the CATC determination may be by thiocyanate (SCN^-), sulfide (S^{2-}), carbonates (HCO_3^-, CO_3^{2-}), nitrite (NO_2^-), oxidants (ClO_4^-, O_3, H_2O_2), bisulfite (HSO_3^-), formaldehyde (HCHO), surfactants, and metals. Method OIA–1677 is either not susceptible to these interferences or contains procedures that eliminate these interferences or mitigate their effects. The reason that this method is much less susceptible to interferences than the approved CATC methods is that the chlorination reaction is not employed. Rather, the aqueous sample passes a gas diffusion membrane through which the HCN diffuses, as explained in greater detail in the later section of this preamble that describes Method OIA–1677. With approval of Method OIA–1677, EPA believes that most of the reported interference problems in the determination of cyanide would be overcome.

Interferences in the CATC methods normally produce an inflated result for cyanide and, in many instances, the measured level exceeds the concentration for total cyanide, potentially providing a more controversial result in some regulatory contexts. Because Method OIA–1677 is nearly immune to the interferences that inflate results from CATC methods, the result of an analysis using Method OIA–1677 will nearly always be lower, and therefore closer to the true value for cyanide than a result from an analysis using a CATC method. The only exception may be for an analysis in which interferences are not present but certain cyanides of nickel, mercury, or silver are present at high concentrations, as described above. Therefore, the tradeoff in use of Method OIA–1677 versus presently approved CATC methods is that, with Method OIA–1677, there is a reduced susceptibility to interferences, whereas with approved CATC methods, there is a somewhat decreased result if certain cyanides of nickel, mercury, or silver are present at high concentrations. EPA believes that the tradeoff heavily favors use of Method OIA–1677 based on the expected susceptibility of CATC methods to interferences combined with the small probability that a cyanide of nickel, mercury, and silver will be present at a high concentration and be the dominant cyanide in a given discharge. Dominance is important because if a cyanide of nickel, mercury, or silver is present at a concentration that is small in comparison to another cyanide present, the effect on the measured cyanide concentration will be diminished in proportion to the concentration relative to the other cyanide.

Because the lowest result for a given cyanide determination can be produced by either Method OIA–1677 or by a presently approved CATC method, dischargers will likely choose the method that produces the lowest result. The adverse environmental impact to choosing presently approved CATC methods is that not all of the nickel, mercury, or silver cyanide will be recovered (and measured), if any of these cyanides are present.

E. Regulatory Effects of Use of Different Methods

A regulatory problem may occur when a sample of a given discharge is split and a discharger chooses Method OIA–1677 and a regulatory authority chooses an approved CATC method (or vice versa) and one result shows a violation of a permit limit and the other does not. EPA believes that the difference can be worked out in technical discussions between the discharger and the regulatory authority based on the data produced. If these data show that an interference was present, Method OIA–1677 will likely produce the lower result and this result should be relied upon. On the other hand, if the discharger knows that nickel, mercury or silver cyanide is present in the discharge in high concentration and is dominant, the result from the CATC method would be appropriate because it is most consistent with the method used for permit development. Further, it is unlikely that a discharger would select Method OIA–1677 if it knew that a cyanide of nickel, mercury, or silver was present at high concentration, unless interferences were so large that they overwhelmed the effect of the greater recovery. The concern would then be that the regulatory authority employed Method OIA–1677, not knowing that a cyanide of nickel, mercury, or silver was present at a high concentration and dominant in the discharge. However, the discharger could inform the regulatory authority of this presence and may rely upon the text in this preamble and in the technical literature to convince the regulatory authority that the violation is a result of the regulatory authority's use of Method OIA–1677. Finally, EPA believes that occurrences of this problem will be rare and it is more likely that use of Method OIA–1677 will produce a lower result because it is nearly interference free.

F. Analysis Time

The reflux distillation procedure required by CATC methods, including setup and measurement, takes approximately two hours to perform. Therefore, determination of CATC takes approximately four hours of analysis time. In contrast, Method OIA–1677 takes approximately two minutes to perform. This difference will be especially significant for laboratories performing many CATC analyses.

III. Summary of Proposed Rule

A. Introduction

This proposed rule would make available at part 136 an additional test procedure for measurement of available cyanide. Currently approved methods for measurement of available cyanide are based on sample chlorination. Method OIA–1677 as proposed today uses a flow injection/ligand exchange technique to measure available cyanide. Although Method OIA–1677 and chlorination methods both measure available cyanide, it is possible that the results produced by the two techniques will vary slightly, as detailed above. EPA offers Method OIA–1677 as another testing procedure for a variety of purposes including: permit applications and compliance monitoring under the National Pollutant Discharge Elimination System (NPDES) under CWA Section 402; ambient water quality monitoring; CWA Section 401 certifications; development of new effluent limitations guidelines, pretreatment standards, and new source performance standards in EPA's water programs; and for general laboratory use. This rulemaking does not propose to repeal any of the currently approved methods that test for available cyanide. For NPDES permits, the permitting authority should decide which method is appropriate for the specific NPDES permit based on the circumstances of the particular effluent measured. If the permitting authority does not specify the method to be used for the determination of available cyanide, a discharger would be able to use Method OIA–1677 or any of the presently approved CATC methods.

B. Summary of Proposed Method OIA–1677

Method OIA–1677 is divided into two parts: sample pretreatment and cyanide quantification via amperometric detection. In the sample pretreatment step, ligand-exchange reagents are

added to a 100–mL sample. The ligand-exchange reagents displace cyanide ions (CN^-) from weak and intermediate strength metallo-cyanide complexes.

In the flow-injection analysis system, a 200–µL aliquot of the pretreated sample is injected into the flow injection manifold. The addition of hydrochloric acid converts cyanide ion to hydrogen cyanide (HCN). The hydrogen cyanide diffuses through a membrane into an alkaline receiving solution where it is converted back to cyanide ion (CN^-). The amount of cyanide ion in the alkaline receiving solution is measured amperometrically with a silver working electrode, silver/silver chloride reference electrode, and platinum counter electrode at an applied potential of zero volt. The current generated in the cell is proportional to the concentration of cyanide in the original sample, as determined by calibration.

C. Comparison of Method OIA–1677 to Current Methods

Methods currently approved for determination of available cyanide all test for CATC. Although they represent the best methods available to date, these methods are prone to matrix interference problems. EPA considers Method OIA–1677 to be a significant addition to the suite of analytical testing procedures for available cyanide because it (1) has greater specificity for cyanide in matrices where interferences have been encountered using currently approved methods, (2) has improved precision and accuracy compared to currently approved CATC cyanide methods, (3) measures available cyanide at lower concentrations, (4) offers improved analyst safety, (5) shortens sample analysis time, and (6) reduces laboratory waste.

Method OIA–1677 is not subject to interferences from organic species. The flow-injection technique of Method OIA–1677 excludes all interferences, except sulfide. Sulfide is eliminated by treating the sample with lead carbonate and removing the insoluble lead sulfide by filtration prior to introduction of the sample to the amperometric cell used for cyanide detection.

Method OIA–1677 was tested against two existing cyanide methods: Method 335.1, an EPA-approved CATC method, and Standard Method (SM) 4500 CN^- I, a weak-acid dissociable (WAD) cyanide method. Comparative recovery and precision data were generated from simple metallo-cyanide species in reagent water. Recovery and precision of each method was comparable for the easily dissociable cyanide species. Method OIA–1677 showed superior precision and recoveries of mercury cyanide complexes.

While Method 335.1 does not specify a method detection limit, colorimetric detection is ''sensitive'' to approximately 5 µg/L. The method detection limit (MDL; described at 40 CFR part 136, Appendix B) is 0.5 µg/L for Method OIA–1677, as determined in a multi-laboratory study.

Method OIA–1677 offers improved analyst safety for two reasons. The first reason centers on the generation of hydrogen cyanide gas, a highly toxic compound. Although the proposed flow-injection analysis (FIA) method and currently approved CATC methods all generate HCN, the currently approved methods generate a larger quantity of gas during distillation in an open distillation system. As such, extra care must be taken to prevent accidental release of HCN into the laboratory atmosphere. Method OIA–1677, because it tests a much smaller sample, generates significantly less HCN. In addition, the gas is contained in a closed system with little possibility for release. The second reason for improved safety centers on the use of hazardous substances. Currently approved CATC methods require use of hazardous substances in the distillation and color developing processes. These hazardous substances include hydrochloric acid, pyridine, barbituric acid, chloramine-T, and pyrazolone. Method OIA–1677 requires only hydrochloric acid at a much lower concentration than is used in CATC procedures.

Method OIA–1677 offers a reduced analysis time which should increase sample throughput in the laboratory. Method OIA–1677 uses an automated mixing of the sample with hydrochloric acid and exposure to the gas diffusion membrane in order for the sample concentration to be determined. This process takes approximately two minutes per sample. As a comparison, Method 335.1 requires a one-hour distillation procedure plus the time necessary to add and develop the sample color to determine the presence of cyanide.

Less laboratory waste is generated in Method 1667 because it requires a much smaller sample size for testing. Method 335.1 requires handling a sample size of 500 mL for distillation. Method OIA–1677 requires the addition of the ligand exchange reagents to 100 mL of sample, from which 40–250 µL is used for analysis. This reduces the amount of both hazardous sample and toxic reagents that must be handled and subsequently disposed.

D. Quality Control

The quality control (QC) in Method OIA–1677 is more extensive than the QC in currently approved methods for CATC. Method OIA–1677 contains all of the standardized QC tests proposed in EPA's streamlining initiative (62 FR 14976) and used in the 40 CFR part 136, Appendix A methods. An initial demonstration of laboratory capability is required and consists of: (1) An MDL study to demonstrate that the laboratory is able to achieve the MDL and minimum level of quantification (ML) specified in Method OIA–1677; and (2) an initial precision and recovery (IPR) test, consisting of the analysis of four reagent water samples spiked with the reference standard, to demonstrate the laboratory's ability to generate acceptable precision and recovery. An important component of these and other QC tests required in Method OIA–1677 is the use of mercuric cyanide ($Hg(CN)_2$) as the reference standard for spiking. Mercuric cyanide was chosen because it is fully recovered in Method OIA–1677 and weak-acid dissociable (WAD) methods, whereas mercuric cyanide is only partially recovered in the CATC method. Therefore, mercuric cyanide demonstrates the ability of the ligand-exchange reagents to liberate cyanide from moderately strong metal-cyano complexes. Method OIA–1677 requires the use of standards of known composition and purity, which facilitates more accurate determination of recovery and precision and minimizes variability that may be introduced from spiking substances of unknown or indeterminate purity.

Ongoing QC consists of the following tests that would need to accompany each analytical batch, i.e., a set of 10 samples or less pretreated at the same time:

- Verification of calibration of the flow injection analysis/amperometric detection system, to verify that instrument response has not deviated significantly from that obtained during calibration.
- Analysis of a matrix spike (MS) and matrix spike duplicate (MSD) to demonstrate method accuracy and precision and to monitor matrix interferences. $Hg(CN)_2$ is the reference standard used for spiking.
- Analysis of a laboratory blank to demonstrate freedom from contamination.
- Analysis of a laboratory control sample to demonstrate that the method remains under control.

Method OIA–1677 contains QC acceptance criteria for all QC tests. Compliance with these criteria allows a

data user to evaluate the quality of the results. This increases the reliability of results and provides a means for laboratories and data users to monitor analytical performance, thereby providing a basis for sound, defensible data.

E. Performance-based Measurement System

On October 6, 1997, EPA published a Notice of the Agency's intent to implement a Performance Based Measurement System (PBMS) in all of its programs to the extent feasible (62 FR 52098). The Agency is currently determining the specific steps necessary to implement PBMS in its programs and preparing an implementation plan. Final decisions have not yet been made concerning the implementation of PBMS in water programs. However, EPA is currently evaluating what relevant performance characteristics should be specified for monitoring methods used in the water programs under a PBMS approach to ensure adequate data quality. EPA would then specify performance requirements in its regulations to ensure that any method used for determination of a regulated analyte is at least equivalent to the performance achieved by other currently approved methods. Our expectation is that EPA will publish its PBMS implementation strategy for water programs in the **Federal Register** by the end of calendar year 1998.

Under PBMS, the analyst would have flexibility to modify Method OIA–1677 or to use another method for the determination of available cyanide provided the analyst demonstrates that the performance achieved is at least equivalent to the approved method(s). Since inter-laboratory performance data exists for Method OIA–1677, EPA is proposing that these data be used to specify what performance characteristics would be required for measurement of available cyanide under PBMS. EPA is considering the following performance requirements for the use of modified or alternative methods for the measurement of available cyanide: (1) it measures the same cyanide species; (2) it achieves an MDL that is equal or less than the MDL in Method OIA–1677, or one-third the regulatory compliance level, whichever is greater; and (3) it meets all the performance criteria specified in Table 1 of Method OIA–1677 (initial precision and recovery, on-going precision and recovery, calibration verification, and matrix spike/matrix spike duplicate). The process for demonstrating acceptable performance is specified in Section 9 of the method.

Once EPA has made its final determinations regarding implementation of PBMS in programs under the Clean Water Act, EPA would incorporate specific provisions of PBMS into its regulations, which may include specification of the performance characteristics for measurement of available cyanide and for other regulated pollutants in the water program regulations.

EPA requests public comments on whether the performance characteristics identified above (see Method OIA–1677 for performance criteria) would be relevant performance characteristics under PBMS, and whether there are other performance requirements that the Agency should consider under PBMS for the measurement of available cyanide.

IV. Validation of the Method OIA–1677

ALPKEM developed the version of Method OIA–1677 proposed today according to procedures set forth in EPA's *Guide to Method Flexibility and Approval of EPA Water Methods* (EPA–821–D–96–004, December 1996) which is available from the EPA's Water Resource Center (phone: 202–260–7786). The version of Method OIA–1677 proposed today responds to comments from users of earlier versions, results of the intra- and interlaboratory studies, as well as results from several single-laboratory MDL studies.

A. Intralaboratory Validation Study Results

Prior to interlaboratory testing, ALPKEM conducted a single-laboratory validation study both to refine the method and to demonstrate the method's specificity and selectivity. Those study results, described briefly here, are detailed in the *Report of the Draft Method OIA–1677 Single Laboratory Validation Study* that is included in the docket for this proposed rule.

The single-laboratory study consisted of three sets of tests to establish (1) the ability of Method OIA–1677 to identify the various species of ''free'' metallo-cyanide complexes, (2) the ability of Method OIA–1677 to identify cyanide in the presence of interferences, and (3) the recovery and precision of Method OIA–1677 compared to EPA Method 335.1 and SM 4500 CN–I. To determine Method OIA–1677's identification of ''free'' metallo-cyanide complexes, two different concentrations of 11 different metallo-cyanide complexes were each analyzed individually in triplicate, for a total of 66 analyses. Method OIA–1677 yielded recoveries ranging from 97 to 104 percent for six of the eleven complexes (cadmium, copper, mercury, nickel, silver, and zinc). However, as with the currently approved methods for available cyanide, Method OIA–1677 did not determine cyanide in iron, gold, and cobalt cyanide complexes.

To test the ability of Method OIA–1677's to identify cyanide in the presence of other species, two different concentrations of 11 interferents were analyzed in triplicate for a single cyanide test solution, resulting in a second set of 66 analyses. Even in the presence of these interferents, cyanide recoveries ranged from 99 to 103 percent.

To compare the performance of Method OIA–1677 to the performance of approved methods, 2 different concentrations of the same 11 ''free'' metallo-cyanide complexes given above were analyzed individually in triplicate by the EPA-approved CATC Method 335.1, SM 4500 CN–I, and Method OIA–1677. This resulted in a third set of 66 data points. These results show improved recoveries and reduced relative standard deviations for Method OIA–1677 compared to both the SM 4500 CN–I and the CATC methods for selected analytes. For the mercury cyanide complexes, recovery improved from 59 percent for SM 4500 CN–I to 99 percent for Method OIA–1677. High levels of interferences in the nickel and silver determinations showed similar improvements over the CATC method. However, data for zinc, cadmium, copper were comparable among the three cyanide procedures. There was no recovery and thus no method improvement for cobalt, gold, or iron cyanide complexes.

B. Interlaboratory Validation Study Results

In association with the Analytical Methods Staff (AMS) in EPA's Office of Water, ALPKEM conducted an interlaboratory validation study. Those study results, briefly described here, are detailed in a report titled, *The Interlaboratory Validation of Method OIA–1677,* and are included in the docket for this proposed rule.

The purpose of the interlaboratory study was (1) to confirm the performance of Method OIA–1677 in multiple laboratories, (2) to assess Method OIA–1677 interlaboratory data variability, and (3) to develop Method OIA–1677 QC acceptance criteria.

Nine laboratories participated in the interlaboratory method validation study, working cooperatively as the WAD Cyanide Round Robin Group. Each laboratory analyzed an identical set of nine field samples using Method OIA–1677. These field samples were

collected from nine different effluents ranging from a publicly owned treatment works (POTW) to an industry likely to contain cyanide in its effluent. Each sample was analyzed in triplicate using the FIA procedure for a total of 243 analyses (9 laboratories × 9 samples in triplicate).

Along with the analysis of the field samples, each laboratory performed all required QC analyses, including initial calibration, calibration verification, determination of initial precision and recovery, blank analysis, determination of ongoing precision and recovery (OPR), determination of matrix spike recovery and matrix spike duplicate recovery (MS/MSD) in each sample type, assessment of recovery of cyanide as $Hg(CN)_2$ spiked into samples (ligand-exchange reagent performance check or LERPC). In addition, each laboratory performed an MDL study.

The relative standard deviation (RSD) of results across all laboratories and all samples was 12 percent. The mean sample recoveries across all effluent types tested was 96 percent, and the MS and MSD mean recoveries were 99 percent across all effluent types tested. These results exceed generally accepted norms for analytical chemistry results.

Prior to collection of interlaboratory data, one study participant submitted comments that focused on the difficulty in addition of the proper amounts of WAD A & WAD B ligand-exchange reagents to a sample. The difficulty occurred because of the variability of drop size. The method was modified to designate a specific volume of ligand-exchange reagent rather than a certain number of drops. The modified method was distributed to interlaboratory study participants prior to testing.

C. Development of Quality Control Acceptance Criteria

Data from the interlaboratory study were used to develop QC acceptance criteria for Method OIA–1677. Laboratory procedures and QC calculations are fully described in the interlaboratory study report. Criteria were developed for initial precision and recovery (IPR), ongoing precision and recovery (OPR), and recovery of cyanide as $Hg(CN)_2$ spiked into reagent water samples (ligand-exchange reagent performance check, LERPC). QC acceptance criteria for the IPR, OPR, matrix spike (MS), matrix spike duplicate (MSD), and relative percent difference (RPD) for the MS and MSD were calculated using procedures described in EPA's Streamlining Guide. In addition to those procedures, QC acceptance criteria also were developed for $Hg(CN)_2$ at the upper level of the analytical range. Criteria for this LERPC test were developed according to the same procedure as for the IPR test.

D. Method Detection Limit Studies

Nine single-laboratory MDL studies were performed as part of the effort to determine MDLs and minimum levels (MLs). The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. To determine the MDL, the laboratories were required to follow the procedure in Appendix B to 40 CFR part 136.

In the Appendix B procedure, seven aliquots of reagent water are spiked with the analyte or analytes of interest and analyzed by the proposed method. For the MDL studies, KCN was used as the spiking material. Spike levels were in the range of one to five times the estimated detection limit. Following addition of KCN, cyanide levels in each of the seven aliquots was determined. The MDL was determined to be 0.5 µg/L CN^-.

The minimum level of quantitation (ML) is defined as the level at which the entire analytical system produces a recognizable signal and an acceptable calibration point. The ML is determined by multiplying the MDL by 3.18 and rounding the resulting value to the number nearest to (1, 2, or 5) x 10^n, where n is an integer. The ML for Method OIA–1677 was calculated to be 1.0 µg/L CN^-. However, because this calculated value was below the lowest calibration standard used in the MDL study, the ML was set at the level of that standard, 2.0 µg/L CN^-. Results of the MDL studies, along with the relevant calculations, are detailed in the interlaboratory study report.

V. Status of Currently Approved Methods

This action proposes to make Method OIA–1677 available for measurement of available cyanide. The previously approved methods for analysis of available cyanide, EPA Method 335.1, SM 4500–CN G, and ASTM D2036–91(B), would not be withdrawn or otherwise affected by this regulation. EPA specifically invites comment on this aspect of the proposal, including the possible consequences and solutions if EPA were to withdraw any such methods.

VI. Regulatory Requirements

A. Executive Order 12866

Under Executive Order 12866, (58 FR 51735 (October 4, 1993)) the Agency must determine whether a regulatory action is ''significant'' and therefore subject to OMB review and the requirements of the Executive Order. The Order defines ''significant regulatory action'' as one that is likely to result in a rule that may: (1) have an annual effect on the economy of $100 million or more or adversely affect in a material way the economy, a sector of the economy, productivity, competition, jobs, the environment, public health or safety, or State, local, or tribal governments or communities; (2) create a serious inconsistency or otherwise interfere with an action taken or planned by another agency; (3) materially alter the budgetary impact of entitlements, grants, user fees, or loan programs or the rights and obligations of recipients thereof; or (4) raise novel legal or policy issues arising out of legal mandates, the President's priorities, or the principles set forth in the Executive Order.''

This regulation is not significant because it approves a testing procedure for use in compliance monitoring and data gathering but does not require its use. It has been determined that this rule is not a ''significant regulatory action'' under the terms of Executive Order 12866 and is therefore not subject to OMB review.

B. Unfunded Mandates Reform Act

Title II of the Unfunded Mandates Reform Act of 1995 (UMRA), P.L. 104–4, establishes requirements for Federal agencies to assess the effects of their regulatory actions on State, local, and tribal governments and the private sector. Under section 202 of the UMRA, EPA generally must prepare a written statement, including a cost-benefit analysis, for proposed and final rules with ''Federal mandates'' that may result in expenditures to State, local, and tribal governments, in the aggregate, or to the private sector, of $100 million or more in any one year. Before promulgating an EPA rule for which a written statement is needed, section 205 of the UMRA generally requires EPA to identify and consider a reasonable number of regulatory alternatives and adopt the least costly, most cost-effective or least burdensome alternative that achieves the objectives of the rule. The provisions of section 205 do not apply when they are inconsistent with applicable law. Moreover, section 205 allows EPA to adopt an alternative other than the least costly, most cost-effective or least burdensome alternative if the Administrator publishes with the final rule an explanation why that alternative was not adopted. Before EPA establishes any regulatory requirements that may significantly or uniquely affect small

governments, including tribal governments, it must have developed under section 203 of the UMRA a small government agency plan. The plan must provide for notifying potentially affected small governments, enabling officials of affected small governments to have meaningful and timely input in the development of EPA regulatory proposals with significant Federal intergovernmental mandates, and informing, educating, and advising small governments on compliance with the regulatory requirements.

Today's proposed rule contains no Federal mandates (under the regulatory provisions of title II of the UMRA) for State, local, or Tribal governments or the private sector. The proposed rule would impose no enforceable duty on any State, local or Tribal governments or the private sector. This rule proposes alternative analytical tests procedures which merely standardize the procedures when testing is otherwise required by a regulatory agency. Therefore, the proposed rule is not subject to the requirements of sections 202 and 205 of the UMRA. EPA invites comment on its conclusions regarding whether alternate test procedures constitute a federal mandate.

EPA has determined that this proposed rule contains no regulatory requirements that might significantly or uniquely affect small governments and thus this proposed rule is not subject to the requirements of section 203 of UMRA. This proposed rule would simply approve an additional test procedure for measurements that may be required under the CWA.

C. Regulatory Flexibility Act

Pursuant to section 605(b) of the Regulatory Flexibility Act, 5 U.S.C. 605(b), the Administrator certifies that this rule will not have a significant economic impact on a substantial number of small entities. This regulation simply approves an additional testing procedure for the measurement of available cyanide which may be required in the implementation of the CWA.

D. Paperwork Reduction Act

In accordance with the Paperwork Reduction Act of 1980, 44 U.S.C. 3501 *et seq.*, EPA must submit an information collection request covering information collection requirements in proposed rules to the Office of Management and Budget (OMB) for review and approval. This rule contains no information collection requirements. Therefore, preparation of an information collection request to accompany this rule is unnecessary.

E. National Technology Transfer and Advancement Act of 1995

Under § 12(d) of the National Technology Transfer and Advancement Act (''NTTAA''), the Agency is required to use voluntary consensus standards in its regulatory activities unless to do so would be inconsistent with applicable law or otherwise impractical. Voluntary consensus standards are technical standards (e.g., material specifications, test methods, sampling procedures, business practice, etc.) that are developed or adopted by voluntary consensus standard bodies. Where available and potentially applicable standards are not used by EPA, the Act requires the Agency to provide Congress, through the Office of Management and Budget (OMB), an explanation for the reasons for not using such standards.

Proposal of Method OIA–1677 is the result of a collaborative effort between OI Analytical, a private sector vendor, and EPA. Method OIA–1677 applies the innovative technologies of ligand exchange, flow injection analysis (FIA), and amperometric detection to the determination of available cyanide, a pollutant regulated under the Clean Water Act. Approval of Method OIA–1677 would allow use of these technologies to overcome interference problems commonly encountered in the determination of available cyanide and would thereby provide more reliable results for compliance determinations.

EPA's search of the technical literature revealed that there are no consensus methods for determination of ''available cyanide by flow injection/ligand exchange/amperometry,'' although ASTM is in the balloting process for approval of such a method. The ASTM method may differ slightly from Method OIA–1677. If ASTM approves such a method prior to final action on today's proposal and EPA determines that the ASTM method is suitable for compliance monitoring and other purposes, EPA may take final action to promulgate the ASTM method (without additional invitation for public comment in the **Federal Register**) when the Agency takes final action to promulgate Method OIA–1677 if the ASTM method ultimately developed does not differ significantly from Method OIA–1677. EPA invites public comments on the Agency's proposed method as well as on any other existing, potentially applicable voluntary consensus standards which the Agency should consider for the determination of available cyanide or cyanide amenable to chlorination by flow injection/ligand exchange/amperometry.

F. Executive Order 13045

The Executive Order, ''Protection of Children from Environmental Health Risks and Safety Risks'' (62 FR 19885, April 23, 1997) applies to any rule that EPA determines (1) ''economically significant'' as defined under Executive Order 12866, and (2) concerns an environmental health or safety risk that EPA has reason to believe may have a disproportionate effect on children. If the regulatory action meets both criteria, the Agency must evaluate the environmental health or safety effects of the planned rule on children; and explain why the planned regulation is preferable to other potentially effective and reasonably feasible alternatives considered by the Agency.

EPA interprets the E.O. 13045 as encompassing only those regulatory actions that are risk based or health based, such that the analysis required under section 5–501 of the E.O. has the potential to influence the regulation. This rule is not subject to E.O. 13045 because it does not involve decisions regarding environmental health or safety risks.

VII. Request for Comments

EPA requests public comments and information on this proposed rule. Specifically, EPA invites comment on the appropriateness Method OIA–1677 for cyanide analysis, the utility of Method OIA–1677 for monitoring, the QC acceptance criteria in Method OIA–1677, and the comparability of results with CATC methods and results produced by Method OIA-1677, and EPA's proposed decision not to withdraw other, existing approved methods for determination of available cyanide by CATC.

List of Subjects in 40 CFR Part 136

Environmental protection, Analytical methods, Monitoring, Reporting and record keeping requirements, Waste treatment and disposal, Water pollution control.

Dated: June 29, 1998.

Carol M. Browner,

Administrator.

In consideration of the preceding, USEPA proposes to amend title 40, chapter I of the Code of Federal Regulations as follows:

PART 136—[AMENDED]

1. The authority citation for part 136 continues to read as follows:

Authority: Secs. 301, 304(h), 307, and 501(a) Pub. L. 95–217, Stat. 1566, *et seq.* (33 U.S.C. 1251, *et seq.*) (The Federal Water Pollution Control Act Amendments of 1972

as amended by the Clean Water Act of 1977 and the Water Quality Act of 1987), 33 U.S.C. 1314 and 1361; 86 Stat. 816, Pub. L. 92–500; 91 Stat. 1567, Pub. L. 92–217; Stat. 7, Pub. L. 100–4 (The ''Act'').

2. Section 136.3, paragraph (a), Table IB is amended by revising entry 24 and adding a new footnote 42 to read as follows:

§ 136.3 Identification of test procedures.

(a) * * *

TABLE IB.—LIST OF APPROVED INORGANIC TEST PROCEDURES

Parameter units and method	Reference (method number or page)				
	EPA[1,35]	Standard methods 18th ed.	ASTM	USGS[2]	Other
* *	*	*	*	*	*
24. Available Cyanide, mg/L Cyanide amenable to chlorination (CATC), Manual distillation with $MgCl_2$ followed by titrimetry or spectrophotometry.	.....	335.14500–CN G ..	D2036–91(B)	.....	
Available, Flow injection and ligand exchange, followed by amperometry.	.....	.....	.....	.....	OIA–1677.[42]
* *	*	*	*	*	*

Table IB Notes:

[1] ''Methods for Chemical Analysis of Water and Wastes'', Environmental Protection Agency, Environmental Monitoring Systems Laboratory-Cincinnati (EMSL–C1), EPA–600/4–79–020, Revised March 1983 and 1979 where applicable.

[2] Fishman, M.J., et al, ''Methods for Analysis of Inorganic Substances in Water and Fluvial Sediments,'' U.S. Department of the Interior, Techniques of Water—Resource Investigations of the U.S. Geological Survey, Denver, CO, Revised 1989, unless otherwise stated.

* * * * * * *

[35] Precision and recovery statements for the atomic absorption direct aspiration and graphite furnace methods, and for the spectrophotometric SDDC method for arsenic are provided in Appendix D of the part titled, ''Precision and Recovery Statements for Methods for Measuring Metals''.

* * * * * * *

[42] Cyanide, Available, Method OIA–1677 (Flow Injection Analysis/Ligand Exchange), ALPKEM, a division of OI Analytical, Box 648, Wilsonville, OR 97070.

* * * * * * *

3. In part 136, appendix A is amended by adding Method OIA–1677 following Method 1625 to read as follows:

Appendix A to part 136—Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater

* * * * *

Method OIA–1677, November 1997—Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry

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 (see Section 17.2.1).

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 and the minimum level (ML) is 2.0 µg/L. The dynamic range is approximately 2.0 µg/L (ppb) to 5.0 mg/L (ppm) cyanide ion using a 200 µL 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 for use by analysts experienced with flow injection equipment or under close supervision of such qualified persons.

1.6 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. Requirements for establishing method equivalency are given in Section 9.1.2.

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 aliquot of the pre-treated 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.

2.3 A flow diagram of the FIA system is shown in Figure 1.

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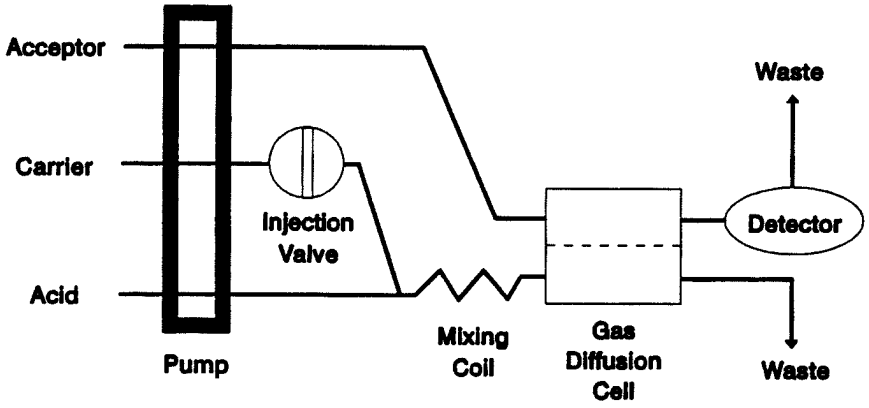

Figure 1. Flow injection Manifold used in the quantification of cyanide in the pretreated sample. Carrier (0.1 M HCl); Acid (0.1 M HCl); Acceptor (0.1 M NaOH).

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3.0 Definitions.

Definitions for terms used in this method are given in the glossary at the end of the method.

4.0 Interferences.

4.1 Solvents, reagents, glassware, and other sample-processing hardware may yield artifacts that affect results. Specific selection of reagents or purification of these reagents may be required.

4.2 All materials used in the analysis shall be demonstrated to be free from interferences under the conditions of analysis by running laboratory blanks as described in Section 9.4.

4.3 Glassware is cleaned by washing in hot water containing detergent, rinsing with tap and reagent water, and drying in an area free from interferences.

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

4.5 Sulfide is a positive interferent in this method (References 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 (Reference 15.7) 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 (Section 8.2.1).

4.6 Though not interferences, substances that react with cyanide should also be removed from samples at time of collection. These substances include water soluble aldehydes that form cyanohydrins and oxidants such as hypochlorite and sulfite. Water soluble aldehydes react with cyanide to form cyanohydrins that are not detected by the analytical system; 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.

4.7 Tests conducted using samples containing large amounts of colloids indicate that cyanide losses are rapid when colloids are present. Filtration can be used to remove colloids, but may have an adverse effect 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.

5.0 Safety.

5.1 The toxicity or carcinogenicity of each compound or reagent used in this method has not been precisely determined; however, each chemical compound should be treated as a potential health hazard. Exposure to these compounds should be reduced to the lowest possible level.

5.2 Cyanides and cyanide solutions.

WARNING: The cyanide ion, hydrocyanic acid, all cyanide salts, and most metal-cyanide complexes are extremely dangerous. As a contact poison, cyanide need not be ingested to produce toxicity. Also, cyanide solutions produce fatally toxic hydrogen cyanide gas when acidified. For these reasons, it is mandatory that work with cyanide be carried out in a well-ventilated hood by properly trained personnel wearing adequate protective equipment.

5.3 Sodium hydroxide solutions.

CAUTION: Considerable heat is generated upon dissolution of sodium hydroxide in water. It may be advisable to cool the container in an ice bath when preparing sodium hydroxide solutions.

5.4 Unknown samples may contain high concentrations of volatile toxic compounds. Sample containers should be opened in a hood and handled with gloves to prevent exposure.

5.5 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses. Additional information on laboratory safety can be found in References 15.8 and 15.9.

6.0 Equipment and Supplies

Note: Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.

6.1 Flow injection analysis (FIA) system—ALPKEM Model 3202 (Reference 15.5), or equivalent, consisting of the following:

6.1.1 Injection valve capable of injecting 40 to 300 µL samples.

6.1.2 Gas diffusion manifold with a microporous Teflon® or polypropylene membrane.

6.1.3 Amperometric detection system with:

6.1.3.1 Silver working electrode.

6.1.3.2 Ag/AgCl reference electrode.

6.1.3.3 Pt/stainless steel counter electrode.

6.1.3.4 Applied potential of 0.0 volt.

6.2 Sampling equipment—Sample bottle, amber glass, 1.1-L, with polytetrafluoroethylene (PTFE)-lined cap. Clean by washing with detergent and water, rinsing with two aliquots of reagent water, and drying by baking at 110–150 °C for one hour minimum.

6.3 Standard laboratory equipment including volumetric flasks, pipettes, syringes, etc. all cleaned, rinsed and dried per bottle cleaning procedure in Section 6.2.

7.0 Reagents and Standards.

7.1 Reagent water—Water in which cyanide and potentially interfering substances are not detected at the MDL of this method. It may be generated by any one of the methods listed below. Reagent water generated by these methods shall be tested for purity utilizing the procedure in Section 11.

7.1.1 Activated carbon—Pass distilled or deionized water through an activated carbon bed (Calgon Filtrasorb-300 or equivalent).

7.1.2 Water purifier—Pass distilled or deionized water through a purifier (Millipore Super Q, or equivalent).

7.2 Sodium hydroxide—ACS reagent grade.

7.3 Potassium cyanide—ACS reagent grade.

7.4 Mercury (II) cyanide, ≥99% purity—Aldrich Chemical Company Catalog No. 20,814–0, or equivalent.

7.5 Silver nitrate—ACS reagent grade. Aldrich Chemical Company Catalog No. 20,913–9, or equivalent.

7.6 Hydrochloric acid—approximately 37%, ACS reagent grade.

7.7 Preparation of stock solutions. Observe the warning in Section 5.2.

7.7.1 Silver nitrate solution, 0.0192 N—Weigh 3.27 g of $AgNO_3$ into a 1-L volumetric flask and bring to the mark with reagent water.

7.7.2 Rhodanine solution, 0.2 mg/mL in acetone—Weigh 20 mg of p-dimethylaminobenzal rhodanine (Aldrich Chemical Co. Catalog No. 11,458–8, or equivalent) in a 100-mL volumetric flask and dilute to the mark with acetone.

7.7.3 Potassium cyanide stock solution, 1000 mg/L

7.7.3.1 Dissolve approximately 2 g (approximately 20 pellets) of sodium hydroxide in approximately 500 mL of reagent water contained in a 1-liter volumetric flask. Observe the caution in Section 5.3. Add 2.51 g of potassium cyanide (Aldrich Chemical Co. Catalog No. 20,781–0, or equivalent), dilute to one liter with reagent water, and mix well. Store KCN solution in an amber glass container at 0–4°C.

7.7.3.2 Standardize the KCN solution (Section 7.7.3.1) by adding 0.5 mL of rhodanine solution (Section 7.7.2) to 25 mL of KCN solution and titrating with $AgNO_3$ solution (Section 7.7.1) until the color changes from canary yellow to a salmon hue. Based on the determined KCN concentration, dilute the KCN solution to an appropriate volume so the final concentration is 1.00 g/L, using the following equation:

Equation 1

$x \times v = 1g/L \times 1L$

Where:

x=concentration of KCN solution determined from titrations

v=volume of KCN solution needed to prepare 1 L of 1 g/L KCN solution

If the concentration is not 1.00 g/L, correct the intermediate and working calibration concentrations accordingly.

7.7.4 1M sodium hydroxide—Dissolve 40 g of sodium hydroxide pellets in approximately 500 mL of reagent water in a 1-liter volumetric flask, observing the caution in Section 5.3. Dilute to one liter with reagent water. Store in an amber bottle at room temperature.

7.8 Secondary standards.

7.8.1 Cyanide, 100 mg/L—Dilute 100.0 mL of cyanide stock solution (Section 7.7.3.2) and 10 mL of 1M sodium hydroxide (Section 7.7.4) to one liter with reagent water (Section 7.1). Store in an amber glass bottle at 0–4°C.

7.8.2 Cyanide, 10 mg/L—Dilute 10.0 mL of cyanide stock solution and 10 mL of 1M sodium hydroxide to one liter with reagent water. Store in an amber glass bottle at 0–4°C.

7.8.3 Cyanide, 1 mg/L—Dilute 1.0 mL of cyanide stock solution and 1 mL of 1M sodium hydroxide to one liter with reagent water. Store in an amber glass bottle at 0–4°C.

7.8.4 Cyanide working calibration standard solutions (2—5000 µg/L as cyanide)—Working calibration standards may be prepared to cover the desired calibration range by adding the appropriate volumes of secondary standards (Sections 7.8.1, 7.8.2, 7.8.3) to 100 mL volumetric flasks that contain 40 mL of reagent water 7.1) and 1 mL of 1M sodium hydroxide (Section 7.7.4). Dilute the solutions to 100 mL with reagent water. Prepare working calibration standards daily. The following table provides the quantity of secondary standard necessary to prepare working standards of the specified concentration.

Working calibration standard concentration (µg/L)	Secondary standard solution volume		
	Secondary standard concentration (section 7.8.3) 1 mg/L	Secondary standard concentration (section 7.8.2) 10 mg/L	Secondary standard concentration (section 7.8.1) 100 mg/L
0.000	.....	.....	.....
2.0	0.200	.....	.....
5.0	0.500	0.050	.....
10.0	1.00	0.100	.....
50.0	5.00	0.500	0.050
100	10.0	1.00	0.100
200	20.0	2.00	0.200
500	50.0	5.00	0.500
1000	.....	10.0	1.00
3000	.....	30.0	3.00
5000	.....	50.0	5.00

If desired, the laboratory may extend the analytical working range by using standards that cover more than one calibration range, so long as the requirements of Section 10.3 are met.

7.9 Sample Preservation Reagents.

7.9.1 The presence of sulfide may result in the conversion of cyanide to thiocyanate. While lead acetate test paper has been recommended for determining the presence of sulfide in samples, the test is generally unreliable and is typically not usable for sulfide concentrations below approximately 1 ppm. The use of lead carbonate (Aldrich Chemical Co. Catalog No. 33,637–8, or equivalent), followed by immediate filtration of the sample is required whenever sulfide ion is present. If the presence of sulfide is suspected but not verifiable from the use of lead acetate test paper, two samples may be collected, one without lead carbonate addition and another with lead carbonate addition followed by immediate filtration. Analyze both samples. If sulfide is present, the preserved sample should contain higher levels of cyanide than the unpreserved sample. Lead acetate test paper may be used, but should be tested for minimum level of sulfide detection by spiking reagent water aliquots with decreasing levels of sulfide and determining the lowest level of sulfide detection attainable. The spiked samples are tested with lead acetate test paper moistened with acetate buffer solution. The buffer solution is prepared by dissolving 146 g anhydrous sodium acetate, or 243 g sodium acetate trihydrate in 400 mL of reagent water, followed by addition of 480 g concentrated acetic acid. Dilute the solution to 1 L with reagent water. Each new batch of test paper and/or acetate buffer should be tested to determine the lowest level of sulfide ion detection prior to use.

7.9.2 Ethylenediamine solution—In a 100 mL volumetric flask, dilute 3.5 mL pharmaceutical-grade anhydrous ethylenediamine (Aldrich Chemical Co. Catalog No. 24,072–9, or equivalent) with reagent water.

7.9.3 Ascorbic acid—Crystals—Aldrich Chemical Co. Catalog No. 26,855–0, or equivalent.

7.10 FIA Reagents.

7.10.1 Carrier and acid reagent (0.1M hydrochloric acid)—Dilute 8 mL of concentrated hydrochloric acid to one liter with reagent water.

7.10.2 Acceptor stock solution (5M sodium hydroxide)—Dissolve 200 grams of sodium hydroxide in 700 mL of reagent water with stirring, observing the caution in Section 5.3. Dilute to one liter with reagent water.

7.10.3 Acceptor reagent (0.1M sodium hydroxide)—Dilute 20 mL of sodium hydroxide solution (Section 7.7.4) to 1000 mL with reagent water.

7.10.4 Ligand-exchange reagent A–ALPKEM part number A001416, or equivalent.

7.10.5 Ligand-exchange reagent B–ALPKEM part number A001417, or equivalent.

7.11 Quality control solutions.

7.11.1 Mercury (II) cyanide stock solution (1000 mg/L as cyanide)—Weigh 0.486 g of mercury (II) cyanide (Section 7.4) in a 100-mL volumetric flask. Add 10–20 mL of reagent water and 1 mL of 1M sodium hydroxide solution (Section 7.7.4). Swirl to mix. Dilute to the mark with reagent water.

7.11.2 Laboratory control sample (LCS)—Place 2.00 mL of the mercury (II) cyanide stock solution (Section 7.11.1) in a 100-mL volumetric flask and dilute to the mark with reagent water to provide a final cyanide concentration of 2.00 mg/L.

8.0 Sample Collection, Preservation, and Storage.

8.1 Sample collection and preservation—Samples are collected using manual (grab) techniques and are preserved immediately upon collection.

8.1.1 Grab sampling—Collect samples in amber glass bottles with PTFE-lined caps cleaned according to the procedure in Section 6.2. Immediately after collection, preserve the sample using any or all of the preservation techniques (Section 8.2), followed by adjustment of the sample pH to ≥12 by addition of 1M sodium hydroxide and refrigeration at 0–4°C.

8.1.2 Compositing—Compositing is performed by combining aliquots of grab samples only. Automated compositing equipment may not be used because cyanide may react or degrade during the sampling period. Preserve and refrigerate each grab sample immediately after collection (Sections 8.1.1 and 8.2) until compositing.

8.1.3 Shipment—If the sample will be shipped by common carrier or mail, limit the pH to a range of 12.0–12.3. (See the footnote to 40 CFR 136.3(e), Table II, for the column headed ''Preservation.'')

8.2 Preservation techniques.

8.2.1 Samples containing sulfide ion—Test samples with lead acetate test paper (Section 7.9.1) to determine the presence or absence of sulfide ion. If sulfide ion is present, treat the sample with sufficient solid lead carbonate (Section 7.9.1) to remove sulfide (as evidenced by lead acetate test paper) and immediately filter into another sample bottle to remove precipitated lead sulfide. If sulfide ion is suspected to be present, but its presence is not detected by this test, two samples should be collected. One is treated for the presence of sulfide and immediately filtered, while the second sample is not treated for sulfide. Both samples must be analyzed by the laboratory. (Tests conducted prior to the interlaboratory validation of this method showed significant and rapid losses of cyanides when lead sulfide was allowed to remain in contact with the sample during holding times of three days and less. As a result, the immediate filtration of samples preserved with lead carbonate is essential (Reference 15.6).

8.2.2 Samples containing water soluble aldehydes—Treat samples containing or suspected to contain formaldehyde, acetaldehyde, or other water soluble aldehydes with 20 mL of 3.5% ethylenediamine solution (Section 7.9.2) per liter of sample.

8.2.3 Samples known or suspected to contain chlorine, hypochlorite, and/or sulfite—Treat with 0.6 g of ascorbic acid (Section 7.9.3) per liter of sample. EPA Method 330.4 or 330.5 may be used for the measurement of residual chlorine (Reference 15.1).

8.3 Sample holding time—Maximum holding time for samples preserved as above is 14 days. Unpreserved samples must be analyzed within 24 hours, or sooner if a change in cyanide concentration will occur. (See the footnotes to Table II at 40 CFR 136.3(e).)

9.0 Quality Control.

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 15.9). The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of LCSs and MS/MSDs as a continuing check on performance. Laboratory performance is compared to established performance criteria to determine if the results of the analyses meet the performance characteristics of the method.

9.1.1 The laboratory shall make an initial demonstration of the ability to generate acceptable precision and accuracy with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, and to allow the laboratory to overcome sample matrix interferences, the laboratory is permitted certain options to improve performance or lower the costs of measurements. Alternate determinative techniques, such as the substitution of spectroscopic or immuno-assay techniques, and changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in this method is used, that technique must have a specificity equal to or better than the specificity of the techniques in this method for the analytes of interest.

9.1.2.1 Each time a modification is made to this method, the laboratory is required to repeat the procedure in Section 9.2. If the detection limit of the method will be affected by the change, the laboratory must demonstrate that the MDL is equal to or less than the MDL in Section 1.4 or one-third the regulatory compliance level, whichever is greater. If calibration will be affected by the change, the laboratory must recalibrate the instrument per Section 10.3.

9.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the information in this subsection, at a minimum.

9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and of the quality control officer who witnessed and will verify the analyses and modification.

9.1.2.2.2 A narrative stating the reason(s) for the modification.

9.1.2.2.3 Results from all quality control (QC) tests comparing the modified method to this method including:

(a) calibration (Section 10.3)

(b) calibration verification (Section 9.5)

(c) initial precision and recovery (Section 9.2)

(d) analysis of blanks (Section 9.4)

(e) laboratory control sample (Section 9.6)

(f) matrix spike and matrix spike duplicate (Section 9.3)

(g) MDL (Section 1.4)

9.1.2.2.4 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include:

(a) sample numbers and other identifiers

(b) analysis dates and times

(c) analysis sequence/run chronology

(d) sample weight or volume

(e) sample volume prior to each cleanup step, if applicable

(f) sample volume after each cleanup step, if applicable

(g) final sample volume prior to injection (Sections 10 and 11)

(h) injection volume (Sections 10 and 11)

(i) dilution data, differentiating between dilution of a sample or modified sample (Sections 10 and 11)

(j) instrument and operating conditions

(k) other operating conditions (temperature, flow rates, etc.)

(l) detector (operating condition, etc.)

(m) printer tapes, disks, and other recording of raw data

(n) quantitation reports, data system outputs, and other data necessary to link raw data to the results reported

9.1.3 Analyses of matrix spike and matrix spike duplicate samples are required to demonstrate method accuracy and precision and to monitor matrix interferences (interferences caused by the sample matrix). The procedure and QC criteria for spiking are described in Section 9.3.

9.1.4 Analyses of blanks are required to demonstrate freedom from contamination and that the compounds of interest and interfering compounds have not been carried over from a previous analysis. The procedures and criteria for analysis of a blank are described in Section 9.4.

9.1.5 The laboratory shall, on an ongoing basis, demonstrate through the analysis of the LCS (Section 7.11.2) that the analysis system is in control. This procedure is described in Section 9.6.

9.1.6 The laboratory should maintain records to define the quality of data that is

generated. Development of accuracy statements is described in Sections 9.3.8 and 9.6.3.

9.1.7 Accompanying QC for the determination of cyanide is required per analytical batch. An analytical batch is a set of samples analyzed at the same time, to a maximum of 10 samples. Each analytical batch of 10 or fewer samples must be accompanied by a laboratory blank (Section 9.4), an LCS (Section 9.6), and a matrix spike and matrix spike duplicate (MS/MSD, Section 9.3), resulting in a minimum of five analyses (1 sample, 1 blank, 1 LCS, 1 MS, and 1 MSD) and a maximum of 14 analyses (10 samples, 1 blank, 1 LCS, 1 MS, and 1 MSD) in the batch. If greater than 10 samples are analyzed at one time, the samples must be separated into analytical batches of 10 or fewer samples.

9.2 Initial demonstration of laboratory capability

9.2.1 Method Detection Limit (MDL)—To establish the ability to detect cyanide at low levels, the laboratory shall determine the MDL per the procedure in 40 CFR 136, Appendix B (Reference 15.4) using the apparatus, reagents, and standards that will be used in the practice of this method. An MDL less than or equal to the MDL listed in Section 1.4 must be achieved prior to practice of this method.

9.2.2 Initial Precision and Recovery (IPR)—To establish the ability to generate acceptable precision and accuracy, the laboratory shall perform the following operations:

9.2.2.1 Analyze four samples of the LCS (Section 7.11.2) according to the procedure beginning in Section 10.

9.2.2.2 Using the results of the set of four analyses, compute the average percent recovery (X) and the standard deviation of the percent recovery (s) for cyanide. Use Equation 2 for calculation of the standard deviation of the percent recovery.

Equation 2

$$s = \sqrt{\frac{\sum x^2 - \frac{\left(\sum x\right)^2}{n}}{n-1}}$$

Where:

n = Number of samples

x = Percent recovery in each sample

9.2.3 Compare s and X with the acceptance criteria specified in Table 1. If s exceeds the precision limit or X falls outside the range for recovery, system performance is unacceptable and the problem must be found and corrected before analyses can begin.

9.3 Matrix spike/matrix spike duplicate (MS/MSD)—The laboratory shall spike, in duplicate, a minimum of 10 percent of all samples (one sample in duplicate in each batch of ten samples) from a given discharge.

9.3.1 The concentration of the spike in the sample shall be determined as follows:

9.3.1.1 If, as in compliance monitoring, the concentration of cyanide in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at 1 to 5 times higher than the background concentration of the sample (determined in Section 9.3.2), whichever concentration is higher.

9.3.1.2 If the concentration of cyanide in a sample is not being checked against a limit, the spike shall be at the concentration of the LCS or at 1 to 5 times higher than the background concentration, whichever concentration is higher.

9.3.2 Analyze one sample aliquot out of each set of ten samples from each discharge according to the procedure beginning in Section 11 to determine the background concentration (B) of cyanide.

9.3.2.1 Spike this sample with the amount of mercury (II) cyanide stock solution (Section 7.11.1) necessary to produce a cyanide concentration in the sample of 2 mg/L. If necessary, prepare another stock solution appropriate to produce a level in the sample at the regulatory compliance limit or at 1 to 5 times the background concentration (per Section 9.3.1).

9.3.2.2 Spike two additional sample aliquots with the spiking solution and analyze these aliquots to determine the concentration after spiking (A).

9.3.3 Calculate the percent recovery of cyanide in each aliquot using Equation 3.

Equation 3

$$p = \frac{100\ (A - B)}{T}$$

Where:

P = Percent recovery

A = Measured concentration of cyanide after spiking

B = Measured background concentration of cyanide

T = True concentration of the spike

9.3.4 Compare the recovery to the QC acceptance criteria in Table 1. If recovery is outside of the acceptance criteria, and the recovery of the LCS in the ongoing precision and recovery test (Section 9.6) for the analytical batch is within the acceptance criteria, an interference is present. In this case, the result may not be reported for regulatory compliance purposes.

9.3.5 If the results of both the MS/MSD and the LCS test fail the acceptance criteria, the analytical system is judged to be out of control. In this case, the problem shall be identified and corrected, and the analytical batch reanalyzed.

9.3.6 Calculate the relative percent difference (RPD) between the two spiked sample results (Section 9.3, not between the two percent recoveries) using Equation 4.

Equation 4

$$RPD = \frac{\left|D_1 - D_2\right|}{\left(D_1 + D_2\right)/2} \times 100SC$$

Where:

RPD = Relative percent difference

D_1 = Concentration of cyanide in the spiked sample

D_2 = Concentration of cyanide in the spiked duplicate sample

9.3.7 Compare the precision to the RPD criteria in Table 1. If the RPD is greater than the acceptance criteria, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected, and the analytical batch reanalyzed.

9.3.8 As part of the QC program for the laboratory, method precision and accuracy for samples should be assessed and records should be maintained. After the analysis of five spiked samples in which the recovery passes the test in Section 9.3.4, compute the average percent recovery (P_a) and the standard deviation of the percent recovery (s_p). Express the accuracy assessment as a percent recovery interval from $P_a - 2s_p$ to $P_a + 2s_p$. For example, if $P_a = 90\%$ and $s_p = 10\%$ for five analyses, the accuracy interval is expressed as 70—110%. Update the accuracy assessment on a regular basis (e.g., after each five to ten new accuracy measurements).

9.4 Laboratory blanks—Laboratory reagent water blanks are analyzed to demonstrate freedom from contamination.

9.4.1 Analyze a reagent water blank initially (i.e., with the tests in Section 9.2) and with each analytical batch. The blank must be subjected to the same procedural steps as a sample.

9.4.2 If cyanide is detected in the blank at a concentration greater than the ML, analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination.

9.5 Calibration verification—Verify calibration of the analytical equipment before and after each analytical batch of 14 or fewer measurements. (The 14 measurements will normally be 10 samples, 1 reagent blank, 1 LCS, 1 MS, and 1 MSD). Verification is accomplished by analyzing the mid-range calibration standard and verifying that it is within the QC acceptance criteria for recovery in Table 1. (The concentration of the calibration verification depends on the calibration range being used.) Failure to verify calibration within the acceptance criteria requires recalibration of the analysis system.

9.6 Laboratory control sample (LCS)—To demonstrate that the analytical system is in control, and acceptable precision and accuracy is being maintained with each analytical batch, the laboratory shall perform the following operations.

9.6.1 Analyze a LCS (Section 7.11.2) with each analytical batch according to the procedure in Section 10.

9.6.2 If the results for the LCS are within the acceptance criteria specified in Table 1, analysis of the batch may continue. If, however, the concentration is not within this range, the analytical process is not in control. In this event, correct the problem, repeat the LCS test, and reanalyze the batch.

9.6.3 The laboratory should add results that pass the specification in Section 9.6.2 to IPR and previous LCS data and update QC charts to form a graphic representation of continued laboratory performance. The laboratory should also develop a statement of laboratory data quality for cyanide by calculating the average percent recovery (R) and the standard deviation of the percent recovery (S_r). Express the accuracy as a recovery interval from $R - 2s_r$ to $R + 2s_r$. For example, if $R = 95\%$ and $s_r = 5\%$, the accuracy is 85% to 105%.

9.7 Reference Sample—To demonstrate that the analytical system is in control, the

laboratory should periodically test an external reference sample, such as a Standard Reference Material (SRM) if an SRM is available from the National Institutes of Standards and Technology (NIST). The reference sample should be analyzed quarterly, at a minimum. Corrective action should be taken if the measured concentration significantly differs from the stated concentration.

10.0 Calibration and Standardization.

This section describes the procedure to calibrate and standardize the FIA system prior to cyanide determination.

10.1 Instrument setup.

10.1.1 Set up the FIA system and establish initial operating conditions necessary for determination of cyanide. If the FIA system is computerized, establish a method for multi-point calibration and for determining the cyanide concentration in each sample.

10.1.2 Verify that the reagents are flowing smoothly through the FIA system and that the flow cell is purged of air bubbles.

10.2 Instrument Stabilization

10.2.1 Load a 10 mg/L KCN standard (Section 7.8.2) into the sampling valve and inject into the FIA system.

10.2.2 Continue to inject 10 mg/L KCN standards until 3 successive peak height or area results are within 2% RSD, indicating that the electrode system is stabilized.

10.2.3 Following stabilization, inject the highest concentration calibration standard until 3 successive peak height or area results are within 2% RSD indicating stabilization at the top of the calibration range.

10.3 External standard calibration.

10.3.1 Inject each of a minimum of 3 calibration standards. One of the standards should be at the minimum level (ML) unless measurements are to be made at higher levels. The other concentrations should correspond to the expected range of concentrations found in samples or should define the working range of the FIA system.

10.3.2 Using injections of a constant volume, analyze each calibration standard according to Section 11 and record peak height or area responses against the concentration. The results can be used to prepare a calibration curve. Alternatively, if the ratio of response to amount injected (calibration factor) is constant over the working range (<10% RSD), linearity through the origin can be assumed and the averaged calibration factor (area/concentration) can be used in place of a calibration curve.

11.0 Procedure.

This section describes the procedure for determination of available cyanide using the FIA system.

11.1 Analysis of standards, samples, and blanks.

11.1.1 Ligand-exchange reagent treatment of standards, samples, and blanks.

11.1.2 To 100-mL of cyanide-containing sample (or standard or blank) at pH of approximately 12, add 100 µL of ligand-exchange reagent Part B (Section 7.10.5), 50 µL of ligand-exchange reagent Part A (Section 7.10.4), and mix thoroughly. Load the sample, standard, or blank into the sample loop.

Note: The ligand-exchange reagents, when added to 100 mL of sample at the specified volume, will liberate cyanide from metal complexes of intermediate stability up to 5 mg/L cyanide ion. If higher concentrations are anticipated, add additional ligand-exchange reagent, as appropriate, or dilute the sample.

11.1.3 Inject the sample and begin data collection. When data collection is complete, analyze the next sample, standard or blank in the batch until analyses of all samples in the batch are completed.

12.0 Data Analysis and Calculations.

12.1 Calculate the concentration of material in the sample, standard or blank from the peak height or area using the calibration curve or calibration factor determined in Section 10.3.

12.2 Reporting.

12.2.1 Samples—Report results to three significant figures for cyanide concentrations found above the ML (Section 1.4) in all samples. Report results below the ML as <5 mg/L, or as required by the permitting authority or permit.

12.2.2 Blanks—Report results to three significant figures for cyanide concentrations found above the MDL (Section 1.3). Do not report results below the MDL unless required by the permitting authority or in the permit.

13.0 Method Performance.

13.1 Method detection limit (MDL)—MDLs from nine laboratories were pooled to develop the MDL of 0.5 µg/L given in Section 1.4 (Reference 15.12).

13.2 Data obtained from single laboratory testing of the method are summarized in Table 2 and show recoveries and reproducibility for ''free'' forms of cyanide, including the recovery and reproducibility of silver, nickel, mercurous and mercuric cyanide species. Determination of these species tends to be problematic with other methods for the determination of available cyanide. As it is the case with other methods used for available cyanide, iron cyanide species were not recovered and recoveries for gold and cobalt species were zero or very low. The complete results from the single laboratory study are available in the *Report of the Draft OIA Method 1677 Single Laboratory Validation Study* (Reference 15.11).

13.3 Listed in Table 1 are the QC acceptance criteria developed from an interlaboratory validation study of this method. This study was conducted following procedures specified in the *Guide to Method Flexibility and Approval of EPA Water Methods* (Reference 15.10). In this study, a total of nine laboratories performed analyses for various water matrices. Table 3 shows a summary of the interlaboratory results which include the accuracy and precision data as % recoveries and relative standard deviations. In addition to spikes of easily dissociable cyanides, some samples contained known amounts of cyanides that are not recoverable (e.g., Pt and Fe complexes) and thiocyanate was spiked to one sample to investigate the potential for interference. The complete study results are available in the *Report of the Draft OIA Method 1677 Interlaboratory Validation Study* (Reference 15.12).

14.0 Pollution Prevention and Waste Management.

14.1 It is the laboratory's responsibility to comply with all federal, State, and local regulations governing waste management, particularly the hazardous waste identification rules and land-disposal restrictions. In addition, it is the laboratory's responsibility to protect air, water, and land resources by minimizing and controlling all releases from fume hoods and bench operations. Also, compliance is required with any sewage discharge permits and regulations.

14.2 Samples containing cyanide, certain metals, and acids at a pH of less than 2 are hazardous and must be treated before being poured down a drain or must be handled as hazardous waste.

14.3 For further information on waste management, consult *Less is Better: Laboratory Chemical Management for Waste Reduction,* Section 15.8.

15.0 References.

15.1 Environmental Monitoring Systems Laboratory. EPA Method 335.1. In: *Methods for the Chemical Analysis of Water and Wastes* (EPA/600/4–79–020). Environmental Protection Agency, Cincinnati, Ohio. Revised March 1983.

15.2 American Public Health Association, American Waterworks Association, Water Pollution Control Board. *Methods Section 4500–CN in Standard Methods for the Examination of Water and Wastewater,* 19th Edition. American Public Health Association, Washington, DC, 1995.

15.3 Ingersol, D.; Harris, W.R.; Bomberger, D.C.; Coulson, D.M. *Development and Evaluation Procedures for the Analysis of Simple Cyanides, Total Cyanides, and Thiocyanate in Water and Waste Water* (EPA–600/4–83–054), 1983.

15.4 *Code of Federal Regulations,* Title 40, Part 136, Appendix B. U.S. Government Printing Office, Washington, D.C., 1994.

15.5 ALPKEM CNSolution Model 3202 Manual. Available from ALPKEM, a division of OI Analytical, Box 648, Wilsonville, OR 97070.

15.6 Milosavljevic, E.B.; Solujic, L.; Hendrix, J.L. *Environmental Science and Technology,* Vol. 29, No. 2, 1995, pp 426–430.

15.7 Wilmont, J.C.; Solujic, L.; Milosavljevic, E. B.; Hendrix, J.L.; Reader, W.S. Analyst, June 1996, Vol. 121, pp 799–801. Formation of Thiocyanate During Removal of Sulfide as Lead Sulfide Prior to Cyanide Determination.

15.8 Less is Better: Laboratory Chemical Management for Waste Reduction. Available from the American Chemical Society, Department of Government Regulations and Science Policy, 1155 16th Street, NW, Washington, DC 20036.

15.9 Handbook for Analytical Quality Control in Water and Wastewater Laboratories (EPA–600/4–79–019), USEPA, NERL, Cincinnati, Ohio 45268 (March 1979).

15.10 Guide to Method Flexibility and Approval of EPA Water Methods, December, 1996, (EPA–821–D–96–004). Available from the National Technical Information Service (PB97–117766).

15.11 Report of the Draft OIA Method 1677 Single Laboratory Validation Study, November 1996. Available from ALPKEM, a division of OI Analytical, Box 648, Wilsonville, OR 97070.

15.12 Report of the Draft OIA Method 1677 Interlaboratory Validation Study, March 1997. Available from ALPKEM, a division of OI Analytical, Box 648, Wilsonville, OR 97070.

16.0 Tables

TABLE 1.—QUALITY CONTROL ACCEPTANCE CRITERIA

Criterion	Required recovery range (%)	Precision
Initial precision and recovery	92–122	<5.1% RSD
Ongoing precision and recovery (Laboratory control sample)	82–132	N/A
Calibration verification	86–118	N/A
Matrix spike/matrix spike duplicate	82–130	<11% RPD

TABLE 2.—Species-Dependent Cyanide Recoveries Using Draft Method 1677 [1]

Species	0.20 µg/mL CN^-	2.00 µg/mL CN^-
$[Zn(CN)_4]^{2-}$	97.4 (0.7)	98.5 (0.7)
$[Cd(CN)_4]^{2-}$	100.0 (0.8)	100.0 (0.2)
$[Cu(CN)_4]^{2-}$	100.9 (1.3)	99.0 (0.6)
$[Ag(CN)_4]^{3-}$	101.8 (0.9)	100.0 (0.5)
$[Ni(CN)_4]^{2-}$	104.3 (0.2)	103.0 (0.5)
$[Hg(CN)_4]^{2-}$	100.0 (0.6)	99.0 (0.3)
$Hg(CN)_2$	103.4 (0.4)	98.0 (0.3)
$[Fe(CN)_4]^{4-}$	0.0	0.0
$[Fe(CN)_6]^{3-}$	0.0	0.0
$[Au(CN)_2]^-$	[2] 1.3 (0.0)	0.0
$[Co(CN)_6]^{3-}$	[2] 2.9 (0.0)	[2] 2.0 (0.0)

[1] Values are % recoveries; numbers in parentheses are percent relative standard deviations.
[2] Commercial product contains some free cyanide.

TABLE 3.—CYANIDE RECOVERIES FROM VARIOUS AQUEOUS MATRICES

Sample	Sample CN concentration	Added CN^- [1] concentration	Average % recovery	% RSD
Reagent water w/0.01M NaOH	0 µg/L	100 µg/L as KCN	108	4.0
POTW secondary effluent	3.0 µg/L	100 µg/L as KCN; 2 mg/L as $[Pt(CN)_6]^{4-}$	102	7.0
Petroleum Refinery Secondary Effluent	9.9 µg/L	2 mg/L as KCN; 5 mg/L as $[Fe(CN)_6]^{4-}$	87	21
Coke Plant Secondary Effluent	14.0 µg/L	50 µg/L as KCN	95	4.0
Rolling Mill Direct Filter Effluent	4.0 µg/L	None	80	41
Metals Finishing Indirect Primary Effluent	1.0 µg/L	200 µg/L as KCN; 2 mg/L as KSCN	92	16
Reagent water w/0.01M NaOH	0 µg/L	200 µg/L as KCN	101	8.0
Reagent water w/0.01M NaOH	0 µg/L	10 mg/L as KCN; 10 mg/L as $[Pt(CN)_6]^{4-}$	103	2.0
Mining Tailing Pond Effluent	842 µg/L	4 mg/L as KCN	98	3.0

[1] Cyano-complexes of Pt and Fe were added to the POTW and petroleum refinery effluents, respectively; and thiocyanate was added to the metals finishing effluent to demonstrate that the FI/LE system does not determine these forms of cyanide.

17.0 Glossary of Definitions and Purposes.

The definitions and purposes are specific to this method but have been conformed to common usage as much as possible.

17.1 Units of weights and measures and their abbreviations

17.1.1 Symbols.

°C degrees Celsius
% percent
± plus or minus
≥ greater than or equal to

17.1.2 Alphabetical characters.

g gram
L liter
mg milligram
mg/L milligram per liter
µg microgram
µg/L microgram per liter
µmL milliliter
ppm parts per million
ppb parts per billion
M molar solution

17.2 Definitions.

17.2.1 Available cyanide consists of cyanide ion (CN^-), hydrogen cyanide in water (HCN_{aq}) and the cyano-complexes of zinc, copper, cadmium, mercury, nickel, and silver.

17.2.2 Calibration blank—A 100 mL volume of reagent water treated with the ligand-exchange reagents and analyzed using the FIA procedure.

17.2.3 Calibration standard (CAL)—A solution prepared from the dilution of stock standard solutions. A 100 mL aliquot of each of the CALs are subjected to the analysis procedure. The resulting observations are used to calibrate the instrument response with respect to the analyte concentration.

17.2.4 Discharge—Specific discharge (also known as ''matrix type'') means a sample medium with common characteristics across a given industrial category or industrial subcategory. Examples include: C-stage effluents from chlorine bleach mills in the Pulp, Paper, and Paperboard industrial category; effluent from the continuous casting subcategory of the Iron and Steel industrial category; publicly owned treatment work (POTW) sludge; and in-process streams in the Atlantic and Gulf Coast Hand-shucked Oyster Processing subcategory. Specific discharge also means a discharge with characteristics different from other discharges. Therefore, if there are multiple discharges from a facility all with the same characteristics, these are the same discharge for the purpose of demonstrating equivalency of a method modification. In this context, ''characteristics'' means that results of the matrix spike and matrix spike duplicate (MS/MSD) tests with the unmodified method meet the QC acceptance criteria for recovery and relative percent difference (RPD).

17.2.5 Initial precision and recovery (IPR)—Four aliquots of the LRB spiked with the analytes of interest and used to establish the ability to generate acceptable precision and accuracy. An IPR is performed the first time this method is used and any time the method or instrumentation is modified.

17.2.6 Laboratory control sample (LCS)—An aliquot of LRB to which a quantity of mercury (II) cyanide stock solution is added in the laboratory. The LCS is analyzed like a sample. Its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements.

17.2.7 Laboratory reagent blank (LRB)—An aliquot of reagent water that is treated like a sample including exposure to all glassware, equipment, and reagents that are used with other samples. The LRB is used to determine if the method analyte or other interferences are present in the laboratory environment, reagents, or apparatus.

17.2.8 Matrix spike/matrix spike duplicate (MS/MSD)—An aliquot of an environmental sample to which a quantity of the method analyte is added in the laboratory. MS/MSDs are analyzed like a sample. Their purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentration of the analyte in the sample matrix must be determined in a separate aliquot and the measured values in the MS/MSD corrected for the background concentration.

17.2.9 Minimum level (ML)—The level at which the entire analytical system shall give a recognizable signal and acceptable calibration point, taking into account method specific sample and injection volumes.

17.2.10 Ongoing Precision and Recovery (OPR)—See Laboratory control sample.

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