821R96003

EPA

Method 1636: Determination of Hexavalent Chromium by Ion Chromatography

Printed on Recycled Paper

Acknowledgments

Method 1636 was prepared under the direction of William A. Telliard of the U.S. Environmental Protection Agency's (EPA's) Office of Water (OW), Engineering and Analysis Division (EAD). The method was prepared under EPA Contract 68-C3-0337 by the DynCorp Environmental Programs Division with assistance from Interface, Inc.

The following researchers contributed to the philosophy behind this method. Their contribution is gratefully acknowledged:

Shier Berman, National Research Council, Ottawa, Ontario, Canada
Nicholas Bloom, Frontier Geosciences Inc., Seattle, Washington
Paul Boothe and Gary Steinmetz, Texas A&M University, College Station, Texas
Eric Crecelius, Battelle Marine Sciences Laboratory, Sequim, Washington
Russell Flegal, University of California/Santa Cruz, California
Gary Gill, Texas A&M University at Galveston, Texas
Carlton Hunt and Dion Lewis, Battelle Ocean Sciences, Duxbury, Massachusetts
Carl Watras, Wisconsin Department of Natural Resources, Boulder Junction, Wisconsin
Herb Windom and Ralph Smith, Skidaway Institute of Oceanography, Savannah, Georgia

In addition, the following personnel at the EPA Office of Research and Development's Environmental Monitoring Systems Laboratory in Cincinnati, Ohio, are gratefully acknowledged for the development of the analytical procedures described in this method:

T.D. Martin
J.D. Pfaff
E.J. Arar (DynCorp, formerly Technology Applications, Inc.)
S.E. Long (DynCorp, formerly Technology Applications, Inc.)

Disclaimer

This method has been reviewed and approved for publication by the Engineering and Analysis Division of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Questions concerning this method or its application should be addressed to:

W.A. Telliard
USEPA Office of Water
Analytical Methods Staff
Mail Code 4303
401 M Street, SW
Washington, DC 20460
Phone: 202/260–7120
Fax: 202/260–7185

Introduction

This analytical method was designed to support water quality monitoring programs authorized under the Clean Water Act. Section 304(a) of the Clean Water Act requires EPA to publish water quality criteria that reflect the latest scientific knowledge about the physical fate (e.g., concentration and dispersal) of pollutants, the effects of pollutants on ecological and human health, and the effect of pollutants on biological community diversity, productivity, and stability.

Section 303 of the Clean Water Act requires states to set a water quality standard for each body of water within its boundaries. A state water quality standard consists of a designated use or uses of a waterbody or a segment of a waterbody, the water quality criteria that are necessary to protect the designated use or uses, and an antidegradation policy. These water quality standards serve two purposes: (1) they establish the water quality goals for a specific waterbody, and (2) they are the basis for establishing water quality-based treatment controls and strategies beyond the technology-based controls required by Sections 301(b) and 306 of the Clean Water Act.

In defining water quality standards, the state may use narrative criteria, numeric criteria, or both. However, the 1987 amendments to the Clean Water Act required states to adopt numeric criteria for toxic pollutants (designated in Section 307(a) of the Act) based on EPA Section 304(a) criteria or other scientific data, when the discharge or presence of those toxic pollutants could reasonably be expected to interfere with designated uses.

In some cases, these water quality criteria are as much as 280 times lower than those achievable using existing EPA methods and required to support technology-based permits. Therefore, EPA developed new sampling and analysis methods to specifically address state needs for measuring toxic metals at water quality criteria levels, when such measurements are necessary to protect designated uses in state water quality standards. The latest criteria published by EPA are those listed in the National Toxics Rule (57 *FR* 60848) and the Stay of Federal Water Quality Criteria for Metals (60 *FR* 22228). These rules include water quality criteria for 13 metals, and it is these criteria on which the new sampling and analysis methods are based. Method 1636 was specifically developed to provide reliable measurements of hexavalent chromium at EPA WQC levels using ion chromatography techniques.

In developing these methods, EPA found that one of the greatest difficulties in measuring pollutants at these levels was precluding sample contamination during collection, transport, and analysis. The degree of difficulty, however, is highly dependent on the metal and site-specific conditions. This analytical method, therefore, is designed to provide the level of protection necessary to preclude contamination in nearly all situations. It is also designed to provide the procedures necessary to produce reliable results at the lowest possible water quality criteria published by EPA. In recognition of the variety of situations to which this method may be applied, and in recognition of continuing technological advances, the method is performance based. Alternative procedures may be used, so long as those procedures are demonstrated to yield reliable results.

Requests for additional copies should be directed to:

US EPA NCEPI
11029 Kenwood Road
Cincinnati, OH 45242
513/489-8190

Note: This method is intended to be performance based, and the laboratory is permitted to omit any step or modify any procedure if *all* performance requirements set forth in this method are met. The laboratory is *not* allowed to omit any quality control analyses. The terms "must," "may," and "should" are included throughout this method and are intended to illustrate the importance of the procedures in producing verifiable data at water quality criteria levels. The term "must" is used to indicate that researchers in trace metals analysis have found certain procedures essential in successfully analyzing samples and avoiding contamination; however, these procedures can be modified or omitted if the laboratory can demonstrate that data quality is not affected.

Method 1636

Determination of Hexavalent Chromium by Ion Chromatography

1.0 Scope and Application

1.1 This method is for the determination of dissolved hexavalent chromium (as CrO_4^{2-}) in ambient waters at EPA water quality criteria (WQC) levels using ion chromatography (IC). This method was developed by integrating the analytical procedures in EPA Method 218.6 with the quality control (QC) and sample handling procedures necessary to avoid contamination and ensure the validity of analytical results during sampling and analysis for metals at EPA WQC levels. This method contains QC procedures that will ensure that contamination will be detected when blanks accompanying samples are analyzed. This method is accompanied by Method 1669: *Sampling Ambient Water for Determination of Trace Metals at EPA Water Quality Criteria Levels* (the "Sampling Method"). The Sampling Method is necessary to ensure that contamination will not compromise trace metals determinations during the sampling process.

Analyte	Chemical Abstract Services Registry Number (CASRN)
Hexavalent Chromium (as CrO_4^{2-})	18540-29-9

1.2 Table 1 lists the EPA WQC level, the method detection limit (MDL), and the minimum level (ML) for hexavalent chromium (Cr(VI)). Linear working ranges will be dependent on the sample matrix, instrumentation, and selected operating conditions.

1.3 This method is not intended for determination of metals at concentrations normally found in treated and untreated discharges from industrial facilities. Existing regulations (40 *CFR* Parts 400–500) typically limit concentrations in industrial discharges to the mid to high part-per-billion (ppb) range, whereas ambient metals concentrations are normally in the low part-per-trillion (ppt) to low ppb range.

1.4 The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized. This method includes suggestions for improvements in facilities and analytical techniques that should maximize the ability of the laboratory to make reliable trace metals determinations and minimize contamination. These suggestions are given in Section 4.0 and are based on findings of researchers performing trace metals analyses (References 1–8). Additional suggestions for improvement of existing facilities may be found in EPA's *Guidance for Establishing Trace Metals Clean Rooms in Existing Facilities*, which is available from the National Center for Environmental Publications and Information (NCEPI) at the address listed in the introduction to this document.

1.5 Clean and ultraclean—The terms "clean" and "ultraclean" have been applied to the techniques needed to reduce or eliminate contamination in trace metals determinations. These terms are not used in this method because they lack an exact definition. However, the information provided in this method is consistent with the summary guidance on clean and ultraclean techniques (Reference 9).

1.6 This method follows the EPA Environmental Methods Management Council's "Format for Method Documentation" (Reference 10).

1.7 This method is "performance based"; i.e., an alternate procedure or technique may be used, as long as the performance requirements in the method are met. Section 9.1.2 gives details of the tests and documentation required to support and document equivalent performance.

1.8 For dissolved Cr(VI) determinations, samples must be filtered through a 0.45-µm capsule filter at the field site. The Sampling Method describes the filtering procedures. The filtered samples should be preserved in the field; otherwise, samples must be analyzed within 24 h of collection. The Sampling Method details procedures for field preservation.

1.9 Samples containing high levels of anionic species such as sulphate and chloride may cause column overload. Samples containing high levels of organics or sulfides cause rapid reduction of soluble Cr(VI) to Cr(III). Samples must be stored at 4°C and analyzed within 24 h of collection unless preserved with sodium hydroxide.

1.10 This method should be used by analysts experienced in the use of ion chromatography, and should be used only by personnel thoroughly trained in the handling and analysis of samples for determination of metals at EPA WQC levels. A minimum of six months experience with commercial instrumentation is recommended.

1.11 This method is accompanied by a data verification and validation guidance document titled *Guidance on the Documentation and Evaluation of Trace Metals Data Collected for CWA Compliance Monitoring*. Before using this method, data users should state the data quality objectives (DQOs) required for a project.

2.0 Summary of Method

2.1 An aqueous sample is filtered through a 0.45-µm filter and the filtrate is adjusted to a pH of 9 to 9.5 with a concentrated buffer solution. A measured volume of the sample (50–250 µL) is introduced into the ion chromatograph. A guard column removes organics from the sample before the Cr(VI), as CrO_4^{2-}, is separated on a high capacity anion exchange separator column. Postcolumn derivatization of the Cr(VI) with diphenylcarbazide is followed by detection of the colored complex at 530 nm.

3.0 Definitions

3.1 Apparatus—Throughout this method, the sample containers, sampling devices, instrumentation, and all other materials and devices used in sample collection, sample processing, and sample analysis activities will be referred to collectively as the Apparatus.

3.2 Other definitions of terms are given in the glossary (Section 18) at the end of this method.

4.0 Contamination and Interferences

4.1 Preventing ambient water samples from becoming contaminated during the sampling and analytical process constitutes one of the greatest difficulties encountered in trace metals determinations. Over the last two decades, marine chemists have come to recognize that much of the historical data on the concentrations of dissolved trace metals in seawater are erroneously high because the concentrations reflect contamination from sampling and analysis rather than ambient levels. More recently, historical trace metals data collected from freshwater rivers and streams have been shown to be similarly biased because of contamination during sampling and analysis (Reference 11). Therefore, it is imperative that extreme care be taken to avoid contamination when collecting and analyzing ambient water samples for trace metals.

4.2 Samples may become contaminated by numerous routes. Potential sources of trace metals contamination during sampling include metallic or metal-containing labware (e.g., talc gloves which contain high levels of zinc), containers, sampling equipment, reagents, and reagent water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust. Even human contact can be a source of trace metals contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) in the mouths of laboratory personnel can contaminate samples that are directly exposed to exhalation (Reference 3).

4.3 Contamination Control

4.3.1 Philosophy—The philosophy behind contamination control is to ensure that any object or substance that contacts the sample is metal free and free from any material that may contain metals.

4.3.1.1 The integrity of the results produced cannot be compromised by contamination of samples. Requirements and suggestions for control of sample contamination are given in this method and the Sampling Method.

4.3.1.2 Substances in a sample cannot be allowed to contaminate the laboratory work area or instrumentation used for trace metals measurements. Requirements and suggestions for protecting the laboratory are given in this method.

4.3.1.3 Although contamination control is essential, personnel health and safety remain the highest priority. Requirements and suggestions for personnel safety are given in the Sampling Method and Section 5 of this method.

4.3.2 Avoiding contamination—The best way to control contamination is to completely avoid exposure of the sample to contamination in the first place. Avoiding exposure means performing operations in an area known to be free from contamination. Two of the most important factors in avoiding/reducing sample contamination are: (1) an awareness of potential sources of contamination and (2) strict attention to work being done. Therefore it is imperative that the procedures described in this method be carried out by well-trained, experienced personnel.

4.3.3 Use a clean environment—The ideal environment for processing samples is a class 100 clean room (Section 6.1.1). If a clean room is not available, all sample preparation should be performed in a class 100 clean bench or a nonmetal glove box fed by particle-free air or nitrogen. Digestions should be performed in a nonmetal fume hood situated, ideally, in the clean room.

4.3.4 Minimize exposure—The Apparatus that will contact samples, blanks, or standard solutions should be opened or exposed only in a clean room, clean bench, or glove box so that exposure to an uncontrolled atmosphere is minimized. When not being used, the Apparatus should be covered with clean plastic wrap, stored in the clean bench or in a plastic box or glove box, or bagged in clean zip-type bags. Minimizing the time between cleaning and use will also minimize contamination.

4.3.5 Clean work surfaces—Before a given batch of samples is processed, all work surfaces in the hood, clean bench, or glove box in which the samples will be processed should be cleaned by wiping with a lint-free cloth or wipe soaked with reagent water.

4.3.6 Wear gloves—Sampling personnel must wear clean, nontalc gloves (Section 6.6.8) during all operations involving handling of the Apparatus, samples, and blanks. Only clean gloves may touch the Apparatus. If another object or substance is touched, the glove(s) must be changed before again handling the Apparatus. If it is even suspected that gloves have become contaminated, work must be halted, the contaminated gloves removed, and a new pair of clean gloves put on. Wearing multiple layers of clean gloves will allow the old pair to be quickly stripped with minimal disruption to the work activity.

4.3.7 Use metal-free Apparatus—All Apparatus used for determination of metals at ambient water quality criteria levels must be nonmetallic, free of material that may contain metals, or both.

4.3.7.1 Construction materials—Only the following materials should come in contact with samples: fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, polypropylene, polysulfone, or ultrapure quartz. PTFE is less desirable than FEP because the sintered material in PTFE may contain contaminates and is susceptible to serious memory contamination (Reference 6). Fluoropolymer or glass containers should be used for samples that will be analyzed for mercury because mercury vapors can diffuse in or out

of the other materials, resulting either in contamination or low-biased results (Reference 3). Stainless steel is a major source of chromium contamination. All materials, regardless of construction, that will directly or indirectly contact the sample must be cleaned using the procedures described in Section 11 and must be known to be clean and metal free before proceeding.

4.3.7.2 The following materials have been found to contain trace metals and should not contact the sample or be used to hold liquids that contact the sample, *unless* these materials have been shown to be free of the metals of interest at the desired level: Pyrex, Kimax, methacrylate, polyvinylchloride, nylon, and Vycor (Reference 6). In addition, highly colored plastics, paper cap liners, pigments used to mark increments on plastics, and rubber all contain trace levels of metals and must be avoided (Reference 12).

4.3.7.3 Serialization—It is recommended that serial numbers be indelibly marked or etched on each piece of Apparatus so that contamination can be traced, and logbooks should be maintained to track the sample from the container through the labware to injection into the instrument. It may be useful to dedicate separate sets of labware to different sample types; e.g., receiving waters vs. effluents. However, the Apparatus used for processing blanks and standards must be mixed with the Apparatus used to process samples so that contamination of all labware can be detected.

4.3.7.4 The laboratory or cleaning facility is responsible for cleaning the Apparatus used by the sampling team. If there are any indications that the Apparatus is not clean when received by the sampling team (e.g., ripped storage bags), an assessment of the likelihood of contamination must be made. Sampling must not proceed if it is possible that the Apparatus is contaminated. If the Apparatus is contaminated, it must be returned to the laboratory or cleaning facility for proper cleaning before any sampling activity resumes.

4.3.8 Avoid Sources of Contamination—Avoid contamination by being aware of potential sources and routes of contamination.

4.3.8.1 Contamination by carryover—Contamination may occur when a sample containing low concentrations of metals is processed immediately after a sample containing relatively high concentrations of these metals. To reduce carryover, the sample introduction system may be rinsed between samples with dilute acid and reagent water. When an unusually concentrated sample is encountered, it is followed by analysis of a laboratory blank to check for carryover. For samples containing high levels of metals, it may be necessary to acid-clean or replace the connecting tubing or inlet system to ensure that contamination will not affect subsequent measurements. Samples known or suspected to contain the lowest concentration of metals should be analyzed first followed by samples containing higher levels. For instruments containing autosamplers, the laboratory should keep track of which station is used for a given sample. When an unusually high concentration of a metal is detected in a sample, the station used for that sample should be cleaned more thoroughly to prevent contamination of subsequent samples, and the results for subsequent

samples should be checked for evidence of the metal(s) that occurred in high concentration.

4.3.8.2 Contamination by samples—Significant laboratory or instrument contamination may result when untreated effluents, in-process waters, landfill leachates, and other samples containing high concentrations of inorganic substances are processed and analyzed. As stated in Section 1.0, this method is not intended for application to these samples, and samples containing high concentrations should not be permitted into the clean room and laboratory dedicated for processing trace metals samples.

4.3.8.3 Contamination by indirect contact—Apparatus that may not directly come in contact with the samples may still be a source of contamination. For example, clean tubing placed in a dirty plastic bag may pick up contamination from the bag and then subsequently transfer the contamination to the sample. Therefore, it is imperative that every piece of the Apparatus that is directly or indirectly used in the collection, processing, and analysis of ambient water samples be cleaned as specified in Section 11.

4.3.8.4 Contamination by airborne particulate matter—Less obvious substances capable of contaminating samples include airborne particles. Samples may be contaminated by airborne dust, dirt, particles, or vapors from unfiltered air supplies; nearby corroded or rusted pipes, wires, or other fixtures; or metal-containing paint. Whenever possible, sample processing and analysis should be done as far as possible from sources of airborne contamination.

4.4 Interferences which affect the accurate determination of Cr(VI) may come from several sources.

4.4.1 Reduction of Cr(VI) to Cr(III) can occur in the presence of reducing species in an acidic medium. At pH 6.5 or greater, however, CrO_4^{2-}, which is less reactive than $HCrO_4^-$, is the predominant species.

4.4.2 Overloading of the analytical column capacity with high concentrations of anionic species, especially chloride and sulphate, will cause a loss of Cr(VI). The column specified in this method can handle samples containing up to 5% sodium sulphate or 2% sodium chloride (Reference 13). Poor recoveries from fortified samples and tailing peaks are typical manifestations of column overload.

5.0 Safety

5.1 Hexavalent chromium is toxic and a suspected carcinogen and should be handled with appropriate precautions. Extreme care should be exercised when weighing the salt for preparation of the stock standard.

5.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations for the safe handling of the chemicals specified in this method (References 14–17). A reference file of material safety data sheets (MSDSs) should also be available to all personnel involved in the chemical analysis. It is also suggested that the laboratory perform personal hygiene monitoring of each analyst who uses this method and that the results of this monitoring be made available to the analyst. The references and bibliography at the end of Reference 17 are particularly comprehensive in dealing with the general subject of laboratory safety.

5.3 Concentrated nitric and hydrochloric acids present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear protective clothing and safety glasses or a shield for eye protection, and observe proper mixing when working with these reagents.

6.0 Apparatus, Equipment, and Supplies

Disclaimer: The mention of trade names or commercial products in this method is for illustrative purposes only and does not constitute endorsement or recommendation for use by the Environmental Protection Agency. Equivalent performance may be achievable using apparatus and materials other than those suggested here. The laboratory is responsible for demonstrating equivalent performance.

6.1 Facility

6.1.1 Clean room—Class 100, 200-ft^2 minimum, with down-flow, positive-pressure ventilation, air-lock entrances, and pass-through doors.

6.1.1.1 Construction materials—Nonmetallic, preferably plastic sheeting attached without metal fasteners. If painted, paints that do not contain the metal(s) of interest should be used.

6.1.1.2 Adhesive mats—for use at entry points to control dust and dirt from shoes.

6.1.2 Fume hoods—nonmetallic, two minimum, with one installed internal to the clean room.

6.1.3 Clean benches—Class 100, one installed in the clean room; the other adjacent to the analytical instrument(s) for preparation of samples and standards.

6.2 Ion Chromatograph

6.2.1 Instrument equipped with a pump capable of withstanding a minimum backpressure of 2000 psi and of delivering a constant flow in the range of 1–5 mL/min and containing no metal parts in the sample, eluent, or reagent flow path

6.2.2 Helium gas supply (high purity, 99.995%)

6.2.3 Pressurized eluent container, plastic, 1- or 2-L size

6.2.4 Sample loops of various sizes (50–250µL)

6.2.5 A pressurized reagent delivery module with a mixing tee and beaded mixing coil

6.2.6 Guard Column—A column placed before the separator column and containing a sorbent capable of removing strongly absorbing organics and particles that would otherwise damage the separator column (Dionex IonPac NG1 or equivalent).

6.2.7 Separator Column—A column packed with a high capacity anion exchange resin capable of separating CrO_4^{2-} from other sample constituents (Dionex IonPac AS7 or equivalent).

6.2.8 A low-volume, flow-through cell, visible lamp detector containing no metal parts in contact with the eluent flow path. Detection wavelength is at 530 nm.

6.2.9 Recorder, integrator, or computer for receiving analog or digital signals for recording detector response (peak height or area) as a function of time

6.3 Alkaline detergent—Liquinox®, Alconox®, or equivalent.

6.4 pH meter or pH paper

6.5 Analytical balance—with capability to measure to 0.1 mg, for use in weighing solids and for preparing standards

6.6 Labware—For determination of trace levels of elements, contamination and loss are of prime consideration. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area should be designated for trace element sample handling. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching, and (2) depleting element concentrations through adsorption processes. All labware must be metal free. Suitable construction materials are fluoropolymer (FEP, PTFE), conventional or linear polyethylene, polycarbonate, and polypropylene. Fluoropolymer should be used when samples are to be analyzed for mercury. All labware should be cleaned according to the procedure in Section 11.4. Gloves, plastic wrap, storage bags, and filters may all be used new without additional cleaning unless results of the equipment blank pinpoint any of these materials as a source of contamination. In this case, either an alternate supplier must be obtained or the materials must be cleaned.

NOTE: *Chromic acid must not be used for cleaning glassware.*

6.6.1 Glassware—Class A volumetric flasks and a graduated cylinder.

6.6.2 Assorted Class A calibrated pipets

6.6.3 10-mL male luer-lock disposable syringes

6.6.4 0.45-µm syringe filters

6.6.5 Storage bottle—High density polypropylene, 1-L capacity.

6.6.6 Wash bottle—One-piece stem fluoropolymer, with screw closure, 125-mL capacity.

6.6.7 Tongs—For removal of Apparatus from acid baths. Coated metal tongs may not be used.

6.6.8 Gloves—clean, nontalc polyethylene, latex, or vinyl; various lengths. Heavy gloves should be worn when working in acid baths since baths will contain hot, strong acids.

6.6.9 Buckets or basins—5- to 50-L capacity, for acid soaking of the Apparatus.

6.6.10 Brushes—Nonmetallic, for scrubbing Apparatus.

6.6.11 Storage bags—Clean, zip-type, nonvented, colorless polyethylene (various sizes) to store the Apparatus.

6.6.12 Plastic wrap—Clean, colorless polyethylene to store the Apparatus.

6.7 Sampling Equipment—The sampling team may contract with the laboratory or a cleaning facility that is responsible for cleaning, storing, and shipping all sampling devices, sample bottles, filtration equipment, and all other Apparatus used for the collection of ambient water samples. Before the equipment is shipped to the field site, the laboratory or facility must generate an acceptable equipment blank (Section 9.5.3) to demonstrate that the sampling equipment is free from contamination.

6.7.1 Sampling Devices—Before ambient water samples are collected, consideration should be given to the type of sample to be collected and the devices to be used (grab, surface, or subsurface samplers). The laboratory or cleaning facility must clean all devices used for sample collection. The Sampling Method describes various types of samplers. Cleaned sampling devices should be stored in polyethylene bags or wrap.

6.7.2 Sample bottles—Fluoropolymer, conventional or linear polyethylene, polycarbonate, or polypropylene; 500-mL with lids. Cleaned sample bottles should be filled with 0.1% Hcl (v/v) until use.

NOTE: *If mercury is a target analyte, fluoropolymer or glass bottles must be used.*

6.7.3 Filtration Apparatus

6.7.3.1 Filter—Gelman Supor 0.45-µm, 15-mm diameter capsule filter (Gelman 12175, or equivalent).

6.7.3.2 Peristaltic pump—115-V a.c., 12-V d.c., internal battery, variable-speed, single-head (Cole-Parmer, portable, "Masterflex L/S," Catalog No. H-07570-10 drive with Quick Load pump head, Catalog No. H-07021-24, or equivalent).

6.7.3.3 Tubing for use with peristaltic pump—styrene/ethylene/butylene/ silicone (SEBS) resin, approx 3/8-in i.d. by approximately 3 ft (Cole-Parmer size 18, Catalog No. G-06464-18, or approximately 1/4-in i.d., Cole-Parmer size 17, Catalog No. G-06464-17, or equivalent). Tubing is cleaned by soaking in 5–10% Hcl solution for 8–24 h, rinsing with reagent water in a clean bench in a clean room, and drying in the clean bench by purging with metal-free air or nitrogen. After drying, the tubing is double-bagged in clear polyethylene bags, serialized with a unique number, and stored until use.

7.0 Reagents and Standards

Reagents may contain elemental impurities that might affect the integrity of analytical data. A trace amount of chromium is sometimes found in reagent grade salts. Since a concentrated buffer solution is used in this method to adjust the pH of samples, each reagent lot should be tested for the metals of interest by diluting and analyzing an aliquot from the lot using the techniques and instrumentation to be used for analysis of samples. The lot will be acceptable if the concentration of the metal of interest is below the MDL listed in this method. All acids used for this method must be of ultra high-purity grade. Suitable acids are available from a number of manufacturers or may be prepared by sub-boiling distillation.

7.1 Reagents for cleaning Apparatus, sample bottle storage, and sample preservation and analysis

7.1.1 Nitric acid—concentrated (sp gr 1.41), Seastar or equivalent

7.1.2 Nitric acid (1+1)—Add 500 mL concentrated nitric acid to 400 mL of regent water and dilute to 1 L.

7.1.3 Nitric acid (1+9)—Add 100 mL concentrated nitric acid to 400 mL of reagent water and dilute to 1 L.

7.1.4 Hydrochloric acid—concentrated (sp gr 1.19).

7.1.5 Hydrochloric acid (1+1)—Add 500 mL concentrated hydrochloric acid to 400 mL of reagent water and dilute to 1 L.

7.1.6 Hydrochloric acid (1+4)—Add 200 mL concentrated hydrochloric acid to 400 mL of reagent water and dilute to 1 L.

7.1.7 Hydrochloric acid (HCl)—1N trace metal grade

7.1.8 Hydrochloric acid (HCl)—10% wt, trace metal grade

7.1.9 Hydrochloric acid (Hcl)—1% wt, trace metal grade

7.1.10 Hydrochloric acid (Hcl)—0.5% (v/v), trace metal grade

7.1.11 Hydrochloric acid (Hcl)—0.1% (v/v) ultrapure grade

7.1.12 Ammonium hydroxide, NH_4OH, (sp gr 0.902), (CASRN 1336-21-6)

7.1.13 Ammonium sulphate, $(NH_4)_2SO_4$, (CASRN 7783-20-2)

7.1.14 1,5-Diphenylcarbazide, (CASRN 140-22-7)

7.1.15 Methanol, HPLC grade

7.1.16 Sulfuric acid, concentrated (sp gr 1.84)

7.2 Reagent water—Water demonstrated to be free from the metal(s) of interest and potentially interfering substances at the MDL for that metal listed in Table 1. Prepared by distillation, deionization, reverse osmosis, anodic/cathodic stripping voltammetry, or other technique that removes the metal(s) and potential interferent(s).

7.3 Cr(VI) Stock Standard Solution—To prepare a 1000 mg/L solution, dissolve 4.501 g of $Na_2CrO_4.4H_2O$ in reagent water and dilute to 1 L. Transfer to a polypropylene storage container.

7.3.1 Preparation of calibration standards—Fresh calibration standards should be prepared every 2 weeks or as needed. Dilute the stock standard solution to levels appropriate to the operating range of the instrument using reagent water. Before final dilution, the standards should be adjusted to pH 9–9.5 with the buffer solution (Section 7.6). Calibration standards should be prepared at a minimum of three concentrations, one of which must be at the ML (Table 1), and another that must be near the upper end of the linear dynamic range. Calibration standards should be verified initially using a quality control sample (Section 7.8).

7.4 Eluent—Dissolve 33 g of ammonium sulphate in 500 mL of reagent water and add 6.5 mL of ammonium hydroxide. Dilute to 1 L with reagent water.

7.5 Postcolumn Reagent—Dissolve 0.5 g of 1,5-diphenylcarbazide in 100 mL of HPLC grade methanol. Add to about 500 mL of reagent water containing 28 mL of 98% sulfuric acid while stirring. Dilute with reagent water to 1 L in a volumetric flask. Reagent is stable for 4 or 5 days but should be prepared only as needed.

7.6 Buffer Solution—Dissolve 33 g of ammonium sulphate in 75 mL of reagent water and add 6.5 mL of ammonium hydroxide. Dilute to 100 mL with reagent water.

7.7 Blanks—The laboratory should prepare the following types of blanks. A calibration blank is used to establish the analytical calibration curve; and the laboratory (method) blank is used to assess possible contamination from the sample preparation procedure. In addition to these blanks, the laboratory may be required to analyze field blanks (Section 9.5.2) and equipment blanks (Section 9.5.3).

7.7.1 Calibration blank—Consists of reagent water adjusted to pH 9–9.5 with the buffer solution (Section 7.6).

7.7.2 Laboratory blank—Must contain all the reagents in the same volumes as used in processing the samples. The laboratory blank must be carried through the same entire preparation scheme as the samples.

7.8 Quality control sample (QCS)—The QCS should be obtained from a source outside the laboratory. The concentration of the QCS solution analyzed will depend on the sensitivity of the instrument. To prepare the QCS, dilute an appropriate aliquot of analytes to a concentration ≤ 100 µg/L in reagent water and adjust the pH to 9–9.5 with the buffer solution (Section 7.6). The QCS should be analyzed as needed to meet data quality needs, and a fresh solution should be prepared quarterly or more frequently as needed.

7.9 Ongoing precision and recovery (OPR) Sample—To an aliquot of reagent water, add aliquots from the stock standard (Section 7.3) to prepare the OPR. The OPR must be carried through the same entire preparation scheme as the samples.

8.0 Sample Collection, Filtration, Preservation, and Storage

8.1 Before samples are collected, consideration should be given to the type of data required so that appropriate preservation and pretreatment steps can be taken. Filtration and pH adjustment should be performed at the time of sample collection or as soon thereafter as practically possible.

8.2 Sample collection—Samples are collected as described in the Sampling Method.

8.3 Sample filtration—For dissolved Cr(VI), samples and field blanks are filtered through a 0.45-µm capsule filter at the field site. The Sampling Method describes filtering procedures.

8.4 Field preservation is advised for hexavalent chromium to provide sample stability for up to 30 days (Reference 18). Samples are preserved with sodium hydroxide as described in the Sampling Method.

8.5 If the samples are not preserved with sodium hydroxide, they must be analyzed within 24 h of collection.

8.6 Samples should be stored in polyethylene bags at 0–4°C until analysis

9.0 Quality Assurance/Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 19). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with metals of interest to evaluate and document data quality, and analysis of standards and blanks as tests of continued

performance. To determine that results of the analysis meet the performance characteristics of the method, laboratory performance is compared to established performance criteria.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision 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, the analyst is permitted to exercise certain options to eliminate interferences or lower the costs of measurements. These options include alternate digestion, concentration, and cleanup procedures, and changes in instrumentation. Alternate determinative techniques, such as the substitution of a colorimetric technique or changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in the method is used, that technique must have a specificity equal to or better than the specificity of the techniques in the method for the analytes of interest.

9.1.2.1 Each time the method is modified, the analyst is required to repeat the procedure in Section 9.2. If the change will affect the detection limit of the method, the laboratory is required to demonstrate that the MDL (40 *CFR* Part 136, Appendix B) is lower than the MDL for that analyte in this method, or one-third the regulatory compliance level, whichever is higher. If the change will affect calibration, the analyst must recalibrate the instrument according to Section 10.

9.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the following, 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 listing of metals measured, by name and CAS Registry number

9.1.2.2.3 A narrative stating reason(s) for the modification(s)

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

(a) Calibration
(b) Calibration verification
(c) Initial precision and recovery (Section 9.2)
(d) Analysis of blanks
(e) Accuracy assessment

9.1.2.2.5 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, where possible:

(a) Sample numbers and other identifiers
(b) Digestion/preparation or extraction dates
(c) Analysis dates and times
(d) Analysis sequence/run chronology
(e) Sample weight or volume
(f) Volume before each extraction/concentration step
(g) Volume after each extraction/concentration step
(h) Final volume before analysis
(i) Injection volume
(j) Dilution data, differentiating between dilution of a sample or extract
(k) Instrument and operating conditions (make, model, revision, modifications)
(l) Columns (type, resin, etc.)
(m) Operating conditions (background corrections, temperature program, flow rates, etc.)
(n) Detector (type, operating conditions, etc.)
(o) Printer tapes and other recordings of raw data
(p) Quantitation reports, data system outputs, and other data to link raw data to results reported

9.1.3 Analyses of blanks are required to demonstrate freedom from contamination. Section 9.5 describes the required types, procedures, and criteria for analysis of blanks.

9.1.4 The laboratory shall spike at least 10% of the samples with the metal of interest to monitor method performance. This test is described in Section 9.3 of this method. When results of these spikes indicate atypical method performance for samples, an alternative extraction or cleanup technique must be used to bring method performance within acceptable limits. If method performance for spikes cannot be brought within the limits given in this method, the result may not be reported for regulatory compliance purposes.

9.1.5 The laboratory shall, on an ongoing basis, demonstrate through calibration verification and through analysis of the ongoing precision and recovery aliquot that the analytical system is in control. Sections 10.4 and 9.6 describe these procedures.

9.1.6 The laboratory shall maintain records to define the quality of data that are generated. Section 9.3.4 describes the development of accuracy statements.

9.2 Initial demonstration of laboratory capability

9.2.1 Method detection limit—To establish the ability to detect hexavalent chromium, the analyst shall determine the MDL for Cr(VI) according to the procedure in 40 *CFR* 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. The laboratory must produce an MDL that is less than or equal to the MDL listed in Table 1, or one-third the regulatory compliance limit,

whichever is greater. MDLs should be determined when a new operator begins work or whenever, in the judgement of the analyst, a change in instrument hardware or operating conditions would dictate that they be redetermined.

9.2.2 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and recovery, the analyst shall perform the following operations.

9.2.2.1 Analyze four aliquots of reagent water spiked with Cr(VI) at 2–3 times the ML (Table 1), according to the procedures in Section 12. All digestion, extraction, and concentration steps, and the containers, labware, and reagents that will be used with samples must be used in this test.

9.2.2.2 Using results of the set of four analyses, compute the average percent recovery (X) for the Cr(VI) in each aliquot and the standard deviation of the recovery (s) for each metal.

9.2.2.3 Compare s and X with the corresponding limits for initial precision and recovery in Table 2. If s and X meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, s exceeds the precision limit or X falls outside the range for accuracy, system performance is unacceptable. Correct the problem and repeat the test (Section 9.2.2.1).

9.2.3 Linear dynamic range (LDR)—The LDR should be determined by analyzing a minimum of 7 calibration standards ranging in concentration from 1 µg/L to 5,000 µg/L across all sensitivity settings of the spectrophotometer. To normalize responses, divide the response by the sensitivity setting multiplier. Perform the linear regression of normalized response vs. concentration and obtain the constants m and b, where m is the slope of the line and b is the y-intercept. Incrementally analyze standards of higher concentration until the measured absorbance response, R, of a standard no longer yields a calculated concentration, C_c, that is ± 10% of the known concentration, C, where $C_c = (R - b)/m$. That concentration defines the upper limit of the LDR for that instrument and analytical operating conditions. Samples having a concentration that is ≥ 90% of the upper limit of the LDR must be diluted to fall within the bounds of the current calibration curve concentration range and reanalyzed.

9.2.4 Quality control sample (QCS)—When beginning the use of this method, quarterly or as required to meet data quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS (Section 7.8). To verify the calibration standards the determined mean concentration from 3 analyses of the QCS must be within ± 10% of the stated QCS value. If the QCS is not within the required limits, an immediate second analysis of the QCS is recommended to confirm unacceptable performance. If the calibration standards, acceptable instrument performance, or both cannot be verified, the source of the problem must be identified and corrected before proceeding with further analyses.

9.3 Method accuracy—To assess the performance of the method on a given sample matrix, the laboratory must perform matrix spike (MS) and matrix spike duplicate (MSD) sample analyses on 10% of the samples from each site being monitored, or at least one MS sample analysis

and one MSD sample analysis must be performed for each sample batch (samples collected from the same site at the same time, to a maximum of 10 samples), whichever is more frequent. Blanks (e.g., field blanks) may not be used for MS/MSD analysis.

9.3.1 The concentration of the MS and MSD is determined as follows:

9.3.1.1 If, as in compliance monitoring, the concentration of Cr(VI) in the sample is being checked against a regulatory concentration limit, the spike must be at that limit or at 1–5 times the background concentration, whichever is greater.

9.3.1.2 If the concentration is not being checked against a regulatory limit, the concentration must be at 1–5 times the background concentration or at 1–5 times the ML in Table 1, whichever is greater.

9.3.2 Assessing spike recovery

9.3.2.1 Determine the background concentration (B) of Cr(VI) by analyzing one sample aliquot according to the procedure in Section 12.

9.3.2.2 If necessary, prepare a QC check sample concentrate that will produce the appropriate level (Section 9.3.1) in the sample when the concentrate is added.

9.3.2.3 Spike a second sample aliquot with the QC check sample concentrate and analyze it to determine the concentration after spiking (A) of Cr(VI).

9.3.2.4 Calculate each percent recovery (P) as 100(A - B)/T, where T is the known true value of the spike.

9.3.3 Compare the percent recovery (P) for Cr(VI) with the corresponding QC acceptance criteria found in Table 2. If P falls outside the designated range for recovery, the acceptance criteria have not been met.

9.3.3.1 If the acceptance criteria were not met, analyze the ongoing precision and recovery standard (Section 9.6). If the OPR is within limits for Cr(VI) (Table 2), the analytical system is in control and the problem can be attributed to the sample matrix.

9.3.3.2 For samples that exhibit matrix problems, further isolate the metal(s) from the sample matrix using dilution, chelation, extraction, concentration, hydride generation, or other means and repeat the accuracy test (Section 9.3.2).

9.3.3.3 If the recovery for Cr(VI) remains outside the acceptance criteria, the analytical result for Cr(VI) in the unspiked sample is suspect and may not be reported for regulatory compliance purposes.

9.3.4 Recovery for samples should be assessed and records maintained.

9.3.4.1 After the analysis of five samples of a given matrix type (river water, lake water, etc.) for which Cr(VI) passes the tests in Section 9.3.3, compute the

average percent recovery (R) and the standard deviation of the percent recovery (SR). Express the accuracy assessment as a percent recovery interval from R - 2SR to R + 2SR for each matrix. For example, if R = 90% and SR = 10% for five analyses of river water, the accuracy interval is expressed as 70–110%.

9.3.4.2 Update the accuracy assessment for Cr(VI) in each matrix on a regular basis (e.g., after each five to ten new measurements).

9.4 Precision of matrix spike and duplicate

9.4.1 Calculate the relative percent difference (RPD) between the MS and MSD per the equation below using the concentrations found in the MS and MSD. Do not use the recoveries calculated in Section 9.3.2.4 for this calculation because the RPD is inflated when the background concentration is near the spike concentration.

$$RPD = 100\frac{(|D1-D2|)}{(D1+D2)/2}$$

Where:
D1 = concentration of the analyte in the MS sample
D2 = concentration of the analyte in the MSD sample

9.4.2 The relative percent difference between the matrix spike and the matrix spike duplicate must be less than 20%. If this criterion is not met, the analytical system is be judged to be out of control. Correct the problem and reanalyze all samples in the sample batch associated with the MS/MSD that failed the RPD test.

9.5 Blanks—Blanks are analyzed to demonstrate freedom from contamination.

9.5.1 Laboratory (method) blank

9.5.1.1 Prepare a method blank with each sample batch (samples of the same matrix started through the sample preparation process (Section 12) on the same 12-hour shift, to a maximum of 10 samples). To demonstrate freedom from contamination, analyze the blank immediately after analysis of the OPR (Section 9.6).

9.5.1.2 If Cr(VI) or any potentially interfering substance is found in the blank at a concentration equal to or greater than the MDL (Table 1), sample analysis must be halted, the source of the contamination determined, the samples and a new method blank prepared, and the sample batch and fresh method blank reanalyzed.

9.5.1.3 Alternatively, if a sufficient number of blanks (three minimum) are analyzed to characterize the nature of a blank, the average concentration plus two standard deviations must be less than the regulatory compliance level.

9.5.1.4 If the result for a single blank remains above the MDL or if the result for the average concentration plus two standard deviations of three or more blanks exceeds the regulatory compliance level, results for samples associated with those blanks may not be reported for regulatory compliance purposes. Stated another way, results for all initial precision and recovery tests (Section 9.2) and all samples must be associated with an uncontaminated method blank before these results may be reported for regulatory compliance purposes.

9.5.2 Field blank

9.5.2.1 Analyze the field blank(s) shipped with each set of samples (samples collected from the same site at the same time, to a maximum of 10 samples). Analyze the blank immediately before analyzing the samples in the batch.

9.5.2.2 If Cr(VI) or any potentially interfering substance is found in the field blank at a concentration equal to or greater than the ML (Table 1), or greater than one-fifth the level in the associated sample, whichever is greater, results for associated samples may be the result of contamination and may not be reported for regulatory compliance purposes.

9.5.2.3 Alternatively, if a sufficient number of field blanks (three minimum) are analyzed to characterize the nature of the field blank, the average concentration plus two standard deviations must be less than the regulatory compliance level or less than one-half the level in the associated sample, whichever is greater.

9.5.2.4 If contamination of the field blanks and associated samples is known or suspected, the laboratory should communicate this to the sampling team so that the source of contamination can be identified and corrective measures taken before the next sampling event.

9.5.3 Equipment Blanks—Before any sampling equipment is used at a given site, the laboratory or cleaning facility is required to generate equipment blanks to demonstrate that the sampling equipment is free from contamination. Two types of equipment blanks are required: bottle blanks and sampler check blanks.

9.5.3.1 Bottle blanks—After undergoing appropriate cleaning procedures (Section 11.4), bottles should be subjected to conditions of use to verify the effectiveness of the cleaning procedures. A representative set of sample bottles should be filled with reagent water adjusted to a pH 9–9.5 with the buffer solution (Section 7.6) and allowed to stand for a minimum of 24 h. Ideally, the time that the bottles are allowed to stand should be as close as possible to the actual time that sample will be in contact with the bottle. After standing, the water should be analyzed for any signs of contamination. If any bottle shows signs of contamination, the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles recleaned.

9.5.3.2 Sampler check blanks—Sampler check blanks are generated in the laboratory or at the equipment cleaning contractor's facility by processing reagent water

through the sampling devices using the same procedures that are used in the field (see Sampling Method). Therefore, the "clean hands/dirty hands" technique used during field sampling should be followed when preparing sampler check blanks at the laboratory or cleaning facility.

9.5.3.2.1 Sampler check blanks are generated by filling a large carboy or other container with reagent water (Section 7.2) and processing the reagent water through the equipment using the same procedures used in the field (see Sampling Method). For example, manual grab sampler check blanks are collected by directly submerging a sample bottle into the water, filling the bottle, and capping. Subsurface sampler check blanks are collected by immersing the sampler into the water and pumping water into a sample container.

9.5.3.2.2 The sampler check blank must be analyzed using the procedures given in this method. If Cr(VI) or any potentially interfering substance is detected in the blank, the source of contamination or interference must be identified, and the problem corrected. The equipment must be demonstrated to be free from Cr(VI) before the equipment may be used in the field.

9.5.3.2.3 Sampler check blanks must be run on all equipment that will be used in the field. If, for example, samples are to be collected using both a grab sampling device and a subsurface sampling device, a sampler check blank must be run on both pieces of equipment.

9.6 Ongoing precision and recovery

9.6.1 Prepare an ongoing precision and recovery sample (laboratory fortified method blank) identical to the initial precision and recovery aliquots (Section 9.2) with each sample batch (samples of the same matrix started through the sample preparation process (Section 12) on the same 12-hour shift, to a maximum of 10 samples) by spiking an aliquot of reagent water with the metal(s) of interest.

9.6.2 Analyze the OPR sample before analysis of the method blank and samples from the same batch.

9.6.3 Compute the percent recovery of Cr(VI) in the OPR sample.

9.6.4 Compare the concentration to the limits for ongoing recovery in Table 2. If the acceptance criteria are met, system performance is acceptable and analysis of blanks and samples may proceed. If, however, the recovery falls outside of the range given, the analytical processes are not being performed properly. Correct the problem, reprepare the sample batch, and repeat the ongoing precision and recovery test (Section 9.6).

9.6.5 Add results that pass the specifications in Section 9.6.4 to initial and previous ongoing data for Cr(VI) in each matrix. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each matrix type by calculating the average percent recovery (R) and the standard deviation of percent recovery (SR). Express the accuracy as a recovery interval from R - 2SR to R + 2SR. For example, if R = 95% and SR = 5%, the accuracy is 85–105%.

9.7 The specifications contained in this method can be met if the instrument used is calibrated properly and then maintained in a calibrated state. A given instrument will provide the most reproducible results if dedicated to the settings and conditions required for the analyses of metals by this method.

9.8 Depending on specific program requirements, the laboratory may be required to analyze field duplicates collected to determine the precision of the sampling technique. The relative percent difference (RPD) between field duplicates should be less than 20%. If the RPD of the field duplicates exceeds 20%, the laboratory should communicate this to the sampling team so that the source of error can be identified and corrective measures taken before the next sampling event.

10.0 Calibration and Standardization

10.1 Operating conditions—Because of the diversity of instrument hardware, no detailed instrument operating conditions are provided. The analyst is advised to follow the recommended operating conditions provided by the manufacturer. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions satisfy the quality control requirements in this method. Table 3 lists instrument operating conditions that may be used as a guide for analysts in determining instrument configuration and operating conditions. The flow rate of the eluent pump is set at 1.5 mL/min and the pressure of the reagent delivery module adjusted so that the final flow rate of the postcolumn reagent (Section 7.5) from the detector is 2.0 mL/min. This requires manual adjustment and measurement of the final flow rate using a graduated cylinder and a stop watch. A warm-up period of approximately 30 min after the flow rate has been adjusted is recommended, and the flow rate should be checked prior to calibration and sample analysis.

10.2 Injection sample loop size should be chosen based on anticipated sample concentrations and the selected sensitivity setting of the spectrophotometer. The sample volume used to load the sample loop should be at least 10 times the loop size so that all tubing in contact with sample is thoroughly flushed with the new sample to minimize cross-contamination.

10.3 For initial and daily operation, calibrate the instrument according to the instrument manufacturer's recommended procedures using the calibration blank (Section 7.7.1) and calibration standards (Section 7.3.1) prepared at three or more concentrations, one of which must be at the ML (Table 1), and another that must be near the upper end of the linear dynamic range.

10.4 Calibration verification—Immediately following calibration, an initial calibration verification should be performed. Adjustment of the instrument is performed until verification criteria are met. Only after these criteria are met may blanks and samples be analyzed.

10.4.1 Analyze the mid-point calibration standard (Section 10.3).

10.4.2 Compute the percent recovery of Cr(VI) using the calibration curve obtained in the initial calibration.

10.4.3 Compare the recovery with the corresponding limit for calibration verification in Table 2. If all metals meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may continue using the response from the initial calibration. If the value falls outside the range given, system performance is unacceptable. Locate and correct the problem and/or prepare a new calibration check standard and repeat the test (Sections 10.4.1–10.4.3), or recalibrate the system according to Section 10.3.

10.4.4 Calibration must be verified following every ten samples by analyzing the mid-point calibration standard. If the recovery does not meet the acceptance criteria specified in Table 2, analysis must be halted, the problem corrected, and the instrument recalibrated. All samples after the last acceptable calibration verification must be reanalyzed.

10.5 A calibration blank must be analyzed following every calibration verification to demonstrate that there is no carryover of Cr(VI) and that the analytical system is free from contamination. If the concentration of an analyte in the blank result exceeds the MDL, correct the problem, verify the calibration (Section 10.4), and repeat the analysis of the calibration blank.

11.0 Procedures for Cleaning the Apparatus

11.1 All sampling equipment, sample containers, and labware should be cleaned in a designated cleaning area that has been demonstrated to be free of trace element contaminants. Such areas may include class 100 clean rooms as described by Moody (Reference 20), labware cleaning areas as described by Patterson and Settle (Reference 6), or clean benches.

11.2 Materials such as gloves (Section 6.6.8), storage bags (Section 6.6.11), and plastic wrap (Section 6.6.12) may be used new without additional cleaning unless the results of the equipment blank pinpoint any of these materials as a source of contamination. In this case, either an alternate supplier must be obtained or the materials must be cleaned.

11.3 Cleaning procedures—Proper cleaning of the Apparatus is extremely important, because the Apparatus may not only contaminate the samples but may also remove the analytes of interest by adsorption onto the container surface.

NOTE: *If laboratory, field, and equipment blanks (Section 9.5) from Apparatus cleaned with fewer cleaning steps than those detailed below show no levels of analytes above the MDL, those cleaning steps that do not eliminate these artifacts may be omitted if all performance criteria outlined in Section 9 are met.*

11.3.1 Bottles, labware, and sampling equipment

11.3.1.1 Fill a precleaned basin (Section 6.6.9) with a sufficient quantity of a 0.5% solution of liquid detergent (Section 6.3), and completely immerse each piece of ware. Allow to soak in the detergent for at least 30 min.

11.3.1.2 Using a pair of clean gloves (Section 6.6.8) and clean nonmetallic brushes (Section 6.6.10), thoroughly scrub down all materials with the detergent.

11.3.1.3 Place the scrubbed materials in a precleaned basin. Change gloves.

11.3.1.4 Thoroughly rinse the inside and outside of each piece with reagent water until there is no sign of detergent residue (e.g., until all soap bubbles disappear).

11.3.1.5 Change gloves, immerse the rinsed equipment in a hot (50–60°C) bath of concentrated reagent grade HNO_3 (Section 7.1.1) and allow to soak for at least 2 h.

11.3.1.6 After soaking, use clean gloves and tongs to remove the Apparatus and thoroughly rinse with distilled, deionized water (Section 7.2).

11.3.1.7 Change gloves and immerse the Apparatus in a hot (50–60°C) bath of 1N trace metal grade Hcl (Section 7.1.7), and allow to soak for at least 48 h.

11.3.1.8 Thoroughly rinse all equipment and bottles with reagent water. Proceed with Section 11.3.2 for labware and sampling equipment. Proceed with Section 11.3.3 for sample bottles.

11.3.2 Labware and sampling equipment

11.3.2.1 After cleaning, air-dry in a class 100 clean air bench.

11.3.2.2 After drying, wrap each piece of ware or equipment in two layers of polyethylene film.

11.3.3 Fluoropolymer sample bottles—These bottles should be used if mercury is a target analyte.

11.3.3.1 After cleaning, fill sample bottles with 0.1% (v/v) ultrapure Hcl (Section 7.1.11) and cap tightly. To ensure a tight seal, it may be necessary to use a strap wrench.

11.3.3.2 After capping, double-bag each bottle in polyethylene zip-type bags. Store at room temperature until sample collection.

11.3.4 Bottles, labware, and sampling equipment (polyethylene or material other than fluoropolymer)

11.3.4.1 Apply the steps outlined in Sections 11.3.1.1–11.3.1.8 to all bottles, labware, and sampling equipment. Proceed with Section 11.3.4.2 for bottles or Section 11.3.4.3 for labware and sampling equipment.

11.3.4.2 After cleaning, fill each bottle with 0.1% (v/v) ultrapure Hcl (Section 7.1.11). Double-bag each bottle in a polyethylene bag to prevent contamination of the surfaces with dust and dirt. Store at room temperature until sample collection.

11.3.4.3 After rinsing labware and sampling equipment, air-dry in a class 100 clean air bench. After drying, wrap each piece of ware or equipment in two layers of polyethylene film.

NOTE: *Polyethylene bottles cannot be used to collect samples that will be analyzed for mercury at trace (e.g., 0.012 µg/L) levels because of the potential for vapors to diffuse through the polyethylene.*

11.3.4.4 Polyethylene bags—If polyethylene bags need to be cleaned, clean according to the following procedure:

11.3.4.4.1 Partially fill with cold, (1+1) HNO_3 (Section 7.1.2) and rinse with distilled deionized water (Section 7.2).

11.3.4.4.2 Dry by hanging upside down from a plastic line with a plastic clip.

11.3.5 Silicone tubing, fluoropolymer tubing, and other sampling apparatus—Clean any silicone, fluoropolymer, or other tubing used to collect samples by rinsing with 10% Hcl (Section 7.1.8) and flushing with water from the site before sample collection.

11.3.6 Extension pole—Because of its length, it is impractical to submerse the 2-m polyethylene extension pole (used in with the optional grab sampling device) in acid solutions as described above. If such an extension pole is used, a nonmetallic brush (Section 6.6.10) should be used to scrub the pole with reagent water and the pole wiped down with acids described in Section 11.3.4. After cleaning, the pole should be wrapped in polyethylene film.

11.4 Storage—Store each piece or assembly of the Apparatus in a clean, single polyethylene zip-type bag. If shipment is required, place the bagged apparatus in a second polyethylene zip-type bag.

11.5 All cleaning solutions and acid baths should be periodically monitored for accumulation of metals that could lead to contamination. When levels of metals in the solutions become too

high, the solutions and baths should be changed and the old solutions neutralized and discarded in compliance with state and federal regulations.

12.0 Procedures for Sample Preparation and Analysis

12.1 Filtered, pH-adjusted samples at 4°C should be brought to ambient temperature before analysis.

12.2 Initiate instrument operating configuration and calibrate the instrument as described in Section 10.

12.3 Construct a calibration curve of analyte response (peak height or area) vs. analyte concentration over a concentration range of one or two orders of magnitude. The calibration range should bracket the anticipated concentration range of samples. The coefficient of correlation (r) for the curve should be 0.999 or greater.

12.4 Draw into a new, unused syringe (Section 6.6.3) approximately 3 mL of sample. Inject 10X the volume of the sample loop into the injection valve of the IC. Sample concentrations that exceed the calibration range must be diluted and reanalyzed.

12.5 During analysis of samples, the laboratory must comply with the required quality control described in Sections 9 and 10.

13.0 Data Analysis and Calculations

13.1 The sample concentration can be calculated from the calibration curve. Report values in µg/L. Report results at or above the ML for metals found in samples and determined in standards. Report all results for metals found in blanks, regardless of level.

13.2 For data values less than the ML, two significant figures should be used for reporting element concentrations. For data values greater than or equal to the ML, three significant figures should be used.

13.3 The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

14.0 Method Performance

14.1 The method detection limit (MDL) listed in Table 1 and the quality control acceptance criteria listed in Table 2 were validated in a single laboratory (Reference 21) for dissolved hexavalent chromium.

15.0 Pollution Prevention

15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental

management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option. The acids used in this method should be reused as practicable by purifying by electrochemical techniques. The only other chemicals used in this method are the neat materials used in preparing standards. These standards are used in extremely small amounts and pose little threat to the environment when managed properly. To minimize the volume of expired standards to be disposed, standards should be prepared in volumes consistent with laboratory use.

15.2 For information about pollution prevention that may be applied to laboratories and research institutions, consult *Less is Better: Laboratory Chemical Management for Waste Reduction*, available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street NW, Washington DC 20036, 202/872–4477.

16.0 Waste Management

16.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel*, available from the American Chemical Society at the address listed in Section 15.2.

17.0 References

1 Adeloju, S.B.; Bond, A.M. "Influence of Laboratory Environment on the Precision and Accuracy of Trace Element Analysis," *Anal. Chem.* **1985**, *57*, 1728.

2 Berman, S.S.; Yeats, P.A. "Sampling of Seawater for Trace Metals," *CRC Reviews in Analytical Chemistry* **1985**, *16*, 1.

3 Bloom, N.S. "Ultra-Clean Sampling, Storage, and Analytical Strategies for the Accurate Determination of Trace Metals in Natural Waters"; Presented at the 16th Annual EPA Conference on the Analysis of Pollutants in the Environment, Norfolk, VA, May 5, 1993.

4 Bruland, K.W. "Trace Elements in Seawater," *Chemical Oceanography* **1983**, *8*, 157.

5 Nriagu, J.O.; Larson, G.; Wong, H.K.T.; Azcue, J.M. "A Protocol for Minimizing Contamination in the Analysis of Trace Metals in Great Lakes Waters," *J. Great Lakes Research* **1993**, *19*, 175.

6 Patterson, C.C.; Settle, D.M. "Accuracy in Trace Analysis," In *National Bureau of Standards Special Publication 422*; LaFleur, P.D., Ed., U.S. Government Printing Office: Washington, DC, 1976.

7 Fitzgerald, W.F.; Watras, C.J. *Science of the Total Environment* **1989**, *87/88*, 223.

8 Gill, G.A.; Fitzgerald, W.F. *Deep Sea Res.* **1985**, *32*, 287.

9 Prothro, M.G., "Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Metals Criteria"; EPA Memorandum to Regional Water Management and Environmental Services Division Directors, Oct. 1, 1993.

10 "Format for Method Documentation," Distributed by the EPA Environmental Monitoring Management Council, Washington, DC, Nov. 18, 1993.

11 Windom, H.L; Byrd, J.T.; Smith, R.G., Jr.; Huan, F. "Inadequacy of NASQAN Data for Assessing Metal Trends in the Nation's Rivers," *Environ. Sci. Technol.* **1991**, *25*, 1137.

12 Zief, M.; Mitchell, J.W. "Contamination Control in Trace Metals Analysis"; In *Chemical Analysis,* **1976,** Vol. 47, Chapter 6.

13 Dionex Technical Note No. 26, May 1990.

14 "Carcinogens - Working With Carcinogens," Department of Health, Education, and Welfare. Public Health Service. Centers for Disease Control. National Institute for Occupational Safety and Health, Publication No. 77-206, Aug. 1977. Available from the National Technical Information Service (NTIS) as PB-277256.

15 "OSHA Safety and Health Standards, General Industry"; 29 *CFR* 1910, Occupational Safety and Health Administration, OSHA 2206 (revised January 1976).

16 "Safety in Academic Chemistry Laboratories," American Chemical Society Committee on Chemical Safety, 3rd ed., 1979.

17 "Proposed OSHA Safety and Health Standards, Laboratories," Occupational Safety and Health Administration, *Fed. Regist.,* July 24, 1986.

18 Grohse, P. Research Triangle Institute, Institute Drive, Building 6, Research Triangle Park, NC 27709.

19 *Handbook of Analytical Quality Control in Water and Wastewater Laboratories*; U.S. Environmental Protection Agency, EMSL. Cincinnati, OH: March 1979. EPA-600/4-79-019.

20 Moody, J.R. "NBS Clean Laboratories for Trace Element Analysis," *Anal. Chem.* **1982**, *54*, 1358A.

21 "Results of the Validation Study for Determination of Trace Metals at EPA Water Quality Criteria Levels," April 1995. Available from the Sample Control Center (operated by DynCorp), 300 N. Lee Street, Alexandria, VA 22314, 703/519–1140.

18.0 Glossary

Many of the terms and definitions listed below are used in the EPA 1600-series methods, but terms have been cross-referenced to terms commonly used in other methods where possible.

18.1 **Ambient Water**—Waters in the natural environment (e.g., rivers, lakes, streams, and other receiving waters), as opposed to effluent discharges.

18.2 **Analyte**—A metal tested for by the methods referenced in this method. The analytes are listed in Table 1.

18.3 **Apparatus**—The sample container and other containers, filters, filter holders, labware, tubing, pipets, and other materials and devices used for sample collection or sample preparation, and that will contact samples, blanks, or analytical standards.

18.4 **Calibration Blank**—A volume of reagent water acidified with the same acid matrix as in the calibration standards. The calibration blank is a zero standard and is used to calibrate the ICP instrument (Section 7.7.1).

18.5 **Calibration Standard (CAL)**—A solution prepared from a dilute mixed standard and/or stock solutions and used to calibrate the response of the instrument with respect to analyte concentration.

18.6 **Dissolved Analyte**—The concentration of analyte in an aqueous sample that will pass through a 0.45-µm membrane filter assembly before sample acidification (Section 8.3).

18.7 **Equipment Blank**—An aliquot of reagent water that is subjected in the laboratory to all aspects of sample collection and analysis, including contact with all sampling devices and apparatus. The purpose of the equipment blank is to determine if the sampling devices and apparatus for sample collection have been adequately cleaned before shipment to the field site. An acceptable equipment blank must be achieved before the sampling devices and apparatus are used for sample collection. In addition, equipment blanks should be run on random, representative sets of gloves, storage bags, and plastic wrap for each lot to determine if these materials are free from contamination before use.

18.8 **Field Blank**—An aliquot of reagent water that is placed in a sample container in the laboratory, shipped to the field, and treated as a sample in all respects, including contact with the sampling devices and exposure to sampling site conditions, storage, preservation, and all analytical procedures, which may include filtration. The purpose of the field blank is to determine if the field or sample transporting procedures and environments have contaminated the sample.

18.9 **Field Duplicates (FD1 and FD2)**—Two separate samples collected in separate sample bottles at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

18.10 **Initial Precision and Recovery (IPR)**—Four aliquots of the OPR standard analyzed to establish the ability to generate acceptable precision and accuracy. IPRs are performed before a method is used for the first time and any time the method or instrumentation is modified.

18.11 **Instrument Detection Limit (IDL)**—The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of ten replicate measurements of the calibration blank signal at the selected analytical wavelength.

18.12 **Laboratory Blank**—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The laboratory blank is used to determine if method analytes or interferences are present in the laboratory environment, the reagents, or the apparatus (Sections 7.7.2 and 9.5.1).

18.13 **Laboratory Control Sample (LCS)**—See Ongoing Precision and Recovery (OPR) Standard.

18.14 **Laboratory Duplicates (LD1 and LD2)**—Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicates precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

18.15 **Laboratory Fortified Blank (LFB)**—See Ongoing Precision and Recovery (OPR) Standard.

18.16 **Laboratory Fortified Sample Matrix (LFM)**—See Matrix Spike (MS) and Matrix Spike Duplicate (MSD).

18.17 **Laboratory Reagent Blank (LRB)**—See Laboratory Blank.

18.18 **Linear Dynamic Range (LDR)**—The concentration range over which the instrument response to an analyte is linear (Section 9.2.3).

18.19 **Matrix Spike (MS) and Matrix Spike Duplicate (MSD)**—Aliquots of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations (Section 9.3).

18.20 **May**—This action, activity, or procedural step is optional.

18.21 **May Not**—This action, activity, or procedural step is prohibited.

18.22 **Method Blank**—See Laboratory Blank.

18.23 **Method Detection Limit (MDL)**—The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero (Section 9.2.1 and Table 1).

18.24 **Minimum Level (ML)**—The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point (Reference 9).

18.25 **Must**—This action, activity, or procedural step is required.

18.26 **Ongoing Precision and Recovery (OPR) Standard**—A laboratory blank spiked with known quantities of the method analytes. The OPR is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control and to assure that the results produced by the laboratory remain within the method-specified limits for precision and accuracy (Sections 7.9 and 9.6).

18.27 **Preparation Blank**—See Laboratory Blank.

18.28 **Primary Dilution Standard**—A solution containing the analytes that is purchased or prepared from stock solutions and diluted as needed to prepare calibration solutions and other solutions.

18.29 **Quality Control Sample (QCS)**—A sample containing all or a subset of the method analytes at known concentrations. The QCS is obtained from a source external to the laboratory or is prepared from a source of standards different from the source of calibration standards. It is used to check laboratory performance with test materials prepared external to the normal preparation process.

18.30 **Reagent Water**—Water demonstrated to be free from the method analytes and potentially interfering substances at the MDL for that metal in the method.

18.31 **Should**—This action, activity, or procedural step is suggested but not required.

18.32 **Stock Standard Solution**—A solution containing one or more method analytes that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

Table 1

Hexavalent Chromium Analysis Using Method 1636: Lowest Water Quality Criterion, Method Detection Limit, and Minimum Level

Metal	Lowest Ambient Water Quality Criterion (µg/L)[1]	Method Detection Limit (MDL) and Minimum Level (ML); µg/L	
		MDL[2]	ML[3]
Hexavalent Chromium	10	0.23	0.5

Notes:

1. Lowest of the freshwater, marine, or human health WQC at 40 *CFR* Part 131 (57 *FR* 60848 for human health criteria and 60 *FR* 22228 for aquatic criteria). Hardness-dependent freshwater aquatic life criteria also calculated to reflect a hardness of 25 mg/L $CaCO_3$, and all aquatic life criteria have been adjusted to reflect dissolved levels in accordance with the equations provided in 60 *FR* 22228.
2. Method Detection Limit as determined by 40 *CFR* Part 136, Appendix B.
3. Minimum level (ML) calculated by multiplying laboratory-determined MDL by 3.18 and rounding result to nearest multiple of 1, 2, 5, 10, etc. in accordance with procedures used by EAD and described in the EPA *Draft National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-Based Effluent Limitations Set Below Analytical Detection/Quantitation Levels*, March 22, 1994.

Table 2

Quality Control Acceptance Criteria for Performance Tests in EPA Method 1636[1]

Metal	Initial Precision and Recovery (Section 9.2)		Calibration Verification (Section 10.4)	Ongoing Precision and Recovery (Section 9.6)	Spike Recovery (Section 9.3)
	s	X			
Hexavalent Chromium	20	80–120	90–110	79–122	79–122

1. All specifications expressed as percent.

Table 3: Recommended Ion Chromatographic Conditions

Columns:	Guard Column—Dionex IonPac NG1 Separator Column—Dionex IonPac AS7
Eluent:	250 mM $(NH_4)_2SO_4$ 100 mM NH_4OH Flow rate = 1.5 mL/min
Postcolumn Reagent:	2mM Diphenylcarbohydrazide 10% v/v CH_3OH 1N H_2SO_4 Flow rate = 0.5 mL/min
Detector:	Visible 530 nm
Retention Time:	3.8 min