STATE OF NEW MEXICO
BEFORE THE WATER QUALITY CONTROL COMMISSION

IN THE MATTER OF:

PROPOSED AMENDMENTS TO
STANDARDS FOR INTERSTATE AND
INTRASTATE SURFACE WATERS, **No. WQCC 20-51 (R)**
20.6.4 NMAC

THE NEW MEXICO MINING ASSOCIATION'S
NOTICE OF INTENT TO PRESENT TECHNICAL TESTIMONY

Pursuant to 20.1.6.202 NMAC and the Hearing Officer's April 1, 2021 Order Granting Amigos Bravos' Unopposed Motion for Extension of Time to File Notices of Intent to File Direct and Rebuttal Testimony, the New Mexico Mining Association (NMMA) hereby submits this Notice of Intent to Present Technical Testimony at the hearing of this matter, scheduled to commence July 13, 2021.

I. Identity, Qualifications, and Summary of Testimony from the NMMA's Technical Witness

At the hearing of this matter NMMA will present the following technical witness. The NMMA reserves the right to present additional non-technical witnesses as part of its direct presentation, as well as technical and non-technical witnesses in rebuttal or in response to witnesses, statements or evidence of other parties or members of the public:

A. Mr. David Gratson
P.O. Box 29432
Santa Fe, New Mexico 87592

1. Summary of Mr. Gratson's Qualifications and Direct Testimony

Mr. David Gratson is a Senior Technical Chemist with Environmental Standards, Inc. Mr. Gratson is a Certified Environmental Analytical Chemist with over thirty (30) years of applied

environmental chemistry experience. Mr. Gratson has provided analytical chemistry and regulatory expertise to private industry clients throughout the United States, as well as the U.S. Environmental Protection Agency, the Department of Energy and NASA. Mr. Gratson provides project and program level chemistry consulting and quality assurance oversight support for site investigations, permitting, and regulatory compliance. Mr. Gratson holds a Bachelor of Science degree from Allegheny College, and a Master of Science and Engineering degree from the Colorado School of Mines.

Mr. Gratson will provide direct testimony, which includes advance written testimony submitted herewith, about the numerical limits used in several tables within 20.6.4.900 NMAC. Mr. Gratson will explain why the use of three or more significant figures for numerical limits are incongruous with many commercial analytical laboratories' reporting limits.

2. Estimated Length of Mr. Gratson's Direct Testimony

It is estimated that Mr. Gratson's direct testimony will last approximately fifteen (15) minutes, more or less.

II. Materials Referenced by the NMMA's Witness

In addition to the materials that the NMMA may use as exhibits, as listed below and attached, NMMA's witness referenced or reviewed the materials that are on file with the New Mexico Environment Department for the 2021 Triennial Review Proceeding, the public comment draft of the proposed changes to the regulatory text that NMED issued on November 2, 2020 and NMED's Amended Petition dated March 12, 2021, letters and comments submitted to the NMED in response to its public comment draft, the Water Quality Control Commission's docket for this proceeding, and the Water Quality Control Commission's regulations.

III. NMMA's Hearing Exhibits

A. Mr. Gratson's testimony may include presentation of the following exhibits:

1. Advance Written Testimony of David Gratson
2. Resume of David Gratson
3. 40 CFR Part 136, Appendix C: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry Method 200.7
4. United State Environmental Protection Agency, Method 200.7, Revision 4.4: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry

B. U.S. Environmental Protection Agency, *Office of Water Policy and Technical Guidance on the Interpretation and Implementation of Aquatic Life Metals Criteria*, Memo to Water Management Division Directors Environmental Services Division Directors, Regions I-X, October 1993.

C. Yet to be identified exhibits the NMMA may use in rebuttal.

II. <u>Summary of Non-Technical Comments</u>

NMMA recognizes that, pursuant to 20.1.6.202 NMAC, the notice of intent to present technical testimony pertains to technical testimony; however, the NMMA hereby provides notice that it intends to provide or solicit non-technical testimony from witnesses regarding the following issues described below.

A. NMED's Proposed "Climate Change" Definition (20.6.4.7(C)(4) NMAC)

NMMA may present non-technical testimony supporting the deletion of NMED's proposed amendments to 20.6.4.7(C)(4) NMAC. NMED proposes, in 20.6.4.7(C)(4) NMAC, to add a

definition of "climate change" to the surface water regulations. It is unclear why the definition is needed, however, because no substantive standards or requirements set forth in the 20.6.4 regulations, including in NMED's proposed draft, make use of the term "climate change." Instead, the only place NMED's uses the term is in its proposed amendments to 20.6.4.6(D) NMAC, where an objective is stated that the regulations seek to address "inherent threats to water quality due to climate change." The addition of this definition to the 20.6.4 regulations is superfluous and is likely to create unnecessary confusion for regulators and the regulated community.

B. NMED's Proposed "Contaminants of Emerging Concern" Definition (20.6.4.7(C)(7) NMAC)

NMMA may present non-technical testimony supporting the deletion of NMED's proposed amendments to 20.6.4.7(C)(7) NMAC. NMED proposes amending 20.6.4.7(C)(7) NMAC to define a new phrase, "contaminants of emerging concern," to essentially mean "generally chemical compounds that, although suspected to potentially have impacts, do not have regulatory standards, are not routinely monitored for, and the concentrations to which negative impacts are observed have not been fully studied." This open-ended definition, with its vaguely stated and unscientific operative phrase "suspected to potentially have impacts," is troublesome enough by itself. It is highly objectionable when one considers how the phrase is substantively used in NMED's proposed amendments to 20.6.4.13(F)(1) NMAC. That provision, as proposed, would require in relevant part that "surface waters shall be free of toxic pollutants, *including but not limited to contaminants of emerging concern* . . . ." (Emphasis added.) This provision effectively could be construed as adding a broad range of ill-defined and not fully studied contaminants to the scope of "toxic pollutants" under the regulations, and worse, could create a surface water regulatory prohibition for them. There are at least three problems with this proposal. First, it creates a conflict with the actual definition of "toxic pollutant" in existing 20.6.4.7 NMAC. Second, it

arguably provides unfettered discretion for NMED to decide what compounds it believes are "suspected to potentially have impacts" by unstated persons or entities. Third, it puts the regulation of contaminants of emerging concern well out ahead of the science, since by definition the compounds will not have been fully studied.

C. Definition of "Toxic Pollutant" (20.6.4.7(T)(2) NMAC)

NMMA may present non-technical testimony supporting an amendment to the definition of "toxic pollutant." The current definition of "toxic pollutant" set forth in 20.6.4.7(T)(2) NMAC creates regulatory uncertainty. The definition does not provide clarity regarding the pollutants the Department will require dischargers to address and treat as toxic. The current definition of "toxic pollutant" is not consistent with the Clean Water Act and its implementing regulations. Specifically, 40 C.F.R. § 131.11(a)(2) specifies the requirements for toxic pollutant criteria under the CWA. It provides:

> *Toxic pollutants.* States must review water quality data and information on discharges to identify specific water bodies where toxic pollutants may be adversely affecting water quality or the attainment of the designated water use or where the levels of toxic pollutants are at a level to warrant concern and must adopt criteria for such toxic pollutants applicable to the water body sufficient to protect the designated use. *Where a State adopts narrative criteria for toxic pollutants to protect designated uses, the State must provide information identifying the method by which the State intends to regulate point source discharges of toxic pollutants on water quality limited segments based on such narrative criteria. Such information may be included as part of the standards or may be included in documents generated by the State in response to the Water Quality Planning and Management Regulations* (40 CFR part 130).

(Emphasis added).

NMMA supports amending the definition of "toxic pollutant" as follows:

> "Toxic pollutant" means those pollutants or combination of pollutants, ~~including disease-causing agents, that after discharge and upon exposure, ingestion, inhalation or assimilation into any organism, either directly from the environment or indirectly by ingestion through food chains, will cause death, shortened life spans, disease, adverse behavioral changes, reproductive or physiological impairments or physical deformation in such organisms or their offspring~~ <u>listed by the EPA Administrator under section 307(a) of the federal Clean Water Act, 33 U.S.C. § 1317(a) or in the list below.</u>

The proposed definition would give the regulated community certainty about the pollutants it is required to address, provides the Water Quality Control Commission the option of listing additional pollutants and using the certainty of an existing list is consistent with the Water Quality Control Commission's ground water regulations at 20.6.2.7(T)(2) NMAC.

D. Proposed Changes to Use Attainability Analysis (UAA) (20.6.4.15 NMAC)

(i) Possible Testimony Concerning Jurisdictional Waters and Consistency with Federal Regulations

NMMA may present non-technical testimony supporting why NMED (1) should limit the UAA regulation, 20.6.4.15 NMAC, and its associated "highest attainable use" requirements to waters subject to federal Clean Water Act jurisdiction; (2) clarify the application of "highest attainable use" to be consistent with the federal regulations; and (3) clarify instances when no UAA is required consistent with the federal regulations.

NMED explains that some of the proposed changes to its UAA regulation in 20.6.4.15 NMAC are to ensure consistency with federal regulations (presumably the federal water quality standard regulations at 40 C.F.R. Part 131). However, several of the changes are not consistent with the federal regulations. For instance, the UAA regulation purports to apply to surface waters, such as ephemeral and isolated surface water features, that are not subject to federal jurisdiction because they do not qualify as "waters of the United States." In contrast, the federal regulations clarify that "water quality standards" are "provisions of State or Federal law which consist of a designated use or uses for the waters of the United States and water quality criteria for such waters based upon such uses." 40 C.F.R. § 131.3(i).

In addition, NMED has added several provisions that appear to require that in all instances the UAA proponent determine or demonstrate the "highest attainable use" as part of a UAA.

However, the definition of "highest attainable use" in the federal regulations clarifies that "[t]here is no required highest attainable use where the State demonstrates the relevant use specified in section 101(a)(2) of the [federal Clean Water Act] and sub-categories of such a use are not attainable." 40 C.F.R. § 131.3(m) (emphasis added).The federal regulations also clarify instances when no UAA is required. *See, e.g.,* 40 C.F.R. § 131.10(k). There are no such clarifications in NMED's proposed revisions to its UAA regulation.

(ii) Possible Testimony Concerning 20.6.4.15(E) NMAC

NMMA may present testimony supporting amendments to 20.6.4.15(E) NMAC to make this provision, and the UAAs conducted thereunder, consistent with and subject to the same processes and procedures as the UAAs conducted by the Department pursuant to the amended provisions of 20.6.4.15(D) NMAC. The Department's proposed amendments to 20.6.5.15(D) and 20.6.4.15(E) NMAC create unexplained discrepancies between UAAs conducted by the Department and UAAs conducted by an entity other than the Department. For instance, 20.6.4.15(D)(1) NMAC provides the opportunity for an expedited UAA process that is not included in the provisions of 20.6.4.15(E) NMAC. Additionally 20.6.4.15(D)(1) NMAC authorizes the Department to petition the Water Quality Control Commission for removal of a designated use and establishment of a highest attainable use, whereas when a UAA is conducted by an entity other than the Department, the Department or a proponent can petition the Commission to "modify the designated use." *See* 20.6.4.15(E)(5) NMAC.

E. Proposed Amendments to Iron Limit (20.6.4.900(J)(1) NMAC)

As set forth in 20.6.4.900(J)(1) NMAC, NMED has proposed a chronic aquatic life standard for iron of 1000 µg/L. While NMMA supports the implementation of a chronic aquatic life standard for iron, NMMA may present non-technical testimony supporting the use of the

dissolved chronic criteria form of iron instead of the total recoverable form of iron in the 20.6.4.900(J)(1) standards.

Iron is the fourth most abundant element in the earth's crust and is present in measurable amounts in soils and rocks. Streams are watercourses that convey water and sediment derived from the natural erosion of soils and rocks. The mineralized iron present in these sediments is not bioavailable and therefore non-toxic. The use of the total recoverable method dissolves non-toxic mineral phase iron particles found in these sediments, which overestimates the iron that contributes to toxicity. Using the dissolved from of iron aligns with Environmental Protection Agency's Office of Water Metals Policy, which states that the use of dissolved metals is the recommended approach for setting State Water Quality standards because the dissolved fraction more closely approximates the bioavailable fraction of metal in the water column. Additionally, several states including Arizona, Illinois, and Wyoming have adopted dissolved chronic criteria for iron into their water quality standards.

Respectfully Submitted,

MODRALL SPERLING ROEHL HARRIS & SISK, P.A.

By: */s/ Christina C. Sheehan*
Stuart R. Butzier
Christina C. Sheehan
Post Office Box 2168
Albuquerque, NM 87103-2168
Tel: (505) 848-1800
srb@modrall.com
ccs@modrall.com

GALLAGHER & KENNEDY

By: */s/ Dalva Moellenberg*
Dalva Moellenberg
1239 Paseo de Peralta
Santa Fe, NM 87501-2758
Tel: (505) 982-9523
DLM@gknet.com

Certificate of Service

I hereby certify that on May 3, 2021 a copy of the foregoing "Notice of Intent to Present Technical Testimony" was filed with the WQCC hearing clerk via electronic mail to:

Pamela Jones,
Commission Administrator
Water Quality Control Commission
P.O. Box 5469
Santa Fe, NM 87502
Pamela.Jones@state.nm.us

and sent to the following counsel of record via electronic mail:

Annie Maxfield
John Verhuel
Assitants General Counsel
Office of General Counsel
New Mexico Environment Department
121 Tijeras, NE, Suite 1000
Albuquerque, NM 87102
Annie.maxfield@state.nm.us; John.verheul@stat.nm.us

Louis W. Rose
Kari Olson
Montgomery & Andrews, P.A.
P.O. Box 2307
Santa Fe, New Mexico 87504-2307
lrose@montand.com
kolson@montand.com

Maxine Reynolds
Office of Laboratory Counsel
Los Alamos National Laboratory
P.O. Box 1663, MS A187
Los Alamos, NM 87545
mcreynolds@lanl.gov

Tannis Fox
Western Environmental Law Center
208 Paseo del Pueblo Sur, # 602
Taos, NM 87571
fox@westernlaw.org

Silas R. DeRoma
Stephen Jochem
U.S. Department of Energy
National Nuclear Security Administration
Los Alamos Site Office
3741 West Jemez Road
Los Alamos, NM 87544
Silas.deroma@nnsa.doe.gov
Stephen.jochem@nnsa.doe.gov

Robert F. Sanchez
Assistant Attorney General
Office of the Attorney General
P.O. Box 1508
Santa Fe, NM 87504-1508
Rfsanchez@nmag.gov

Kyle Harwood
Luke Pierpoint
Egolf + Ferlic + Martinez + Harwood, LLC
123 W. San Francisco St., Floor 2
Santa Fe, NM 87501
kyle@egolflaw.com; luke@egolflaw.com

Jolene McCaleb
Elizabeth Taylor
San Juan Water Commission
P.O. Box 2540
Corrales, NM 87048-2540
jmccaleb@taylormccaleb.com;etaylor@taylormccaleb.com

MODRALL SPERLING ROEHL HARRIS & SISK, P.A.

By: */s/ Christina C. Sheehan*
Christina C. Sheehan

STATE OF NEW MEXICO
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PROPOSED AMENDMENTS TO
STANDARDS FOR INTERSTATE AND
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20.6.4 NMAC

PRE-FILED TECHNICAL TESTIMONY OF MR. DAVID GRATSON
A WITNESS ON BEHALF OF THE NEW MEXICO MINING ASSOCIATION

I. Introduction To My Testimony

My name is David A. Gratson, I am offering testimony as an expert on behalf of the New Mexico Mining Association (NMMA) in response to the New Mexico Environment Department's (NMED) Petition to Amend the Standards for Interstate and Intrastate Surface Waters (20.6.4 NMAC). This testimony begins with an overview of my credentials. I will then go on to discuss the proposed rulemaking. I will then provide testimony regarding the significant figures for numerical limits set forth in 20.6.4.900 NMAC in the proposed rule. I provide this testimony in opposition to some of the proposed amendments NMED has introduced as part of its rulemaking.

II. Statement of My Qualifications and Relevant Experience

I am currently employed as a Senior Technical Chemist with Environmental Standards Inc. I have provided technical chemistry and environmental data quality consulting for more than twenty (20) years. Prior to entering the consulting field, I performed analytical chemistry in the environmental industry for the US Department of Energy, and with the National Aeronautics and Space Administration (NASA). Since 2004 I have been a Certified Environmental Analytical Chemist with the National Registry of Certified Chemists (NRCC). My curriculum vitae is provided as NMMA Exhibit 2.

III. Introduction to NMED's Proposed Amendments to Standards for Interstate and Intrastate Waters (20.6.4 NMAC)

Numeric criteria in the Standards for Interstate and Intrastate Waters (Standards) are in most cases noted to contact three or fewer significant figures. Numeric criteria at or above 1,000 mg/L or µg/L are shown with no more than two non-zero digits until the Standards employ accounting for water quality parameters such as alkalinity, hardness, and dissolved organic carbon (DOC). Use of more than three significant figures is noted starting at 20.6.4.900 NMAC. Specifically, in 20.6.4.900(I) NMAC where hardness-dependent criteria for metals in the proposed tables of numeric criteria exceed three significant figures. In 20.6.4.900(I)(3) NMAC, the table contains selected values of calculated acute and chronic criteria, in units of µg/L, with more than three significant figures, viz. aluminum (Al) and manganese (Md) at multiple hardness levels, hexavalent chromium Cr(III) Acute 200, 220 mg/L hardness. These values are calculated based upon the equations provided in 20.6.4.900(I)(1) and 20.6.4.900I(2) NMAC where the factors have up to five significant figures; some of these additional digits are carried through the calculation.

IV. NMMA's Concerns With NMED's Proposed Amendments to 20.6.4.900 NMAC

Commercial analytical laboratories that perform measurements of constituents, such as the water contaminants listed in the Standards, have prescriptive reporting procedures that define the number of significant figures to be reported with each parameter. Most commercial laboratories limit the reported value to two, or at most, three significant figures. Using three significant figures adds additional uncertainty to reported values. In fact, some United States Environmental Protection Agency (EPA) methods prescribe reporting to this algorithm. *See* 40 CFR Part 136, Appendix C, Section 12.4, proved as NMMA Exhibit 3. That EPA Method, employed to measure metals applicable to 20.6.4.900 NMAC, uses a three significant figure maximum for reporting data.

The NMMA is concerned that use of more than three significant figures in the Standards will result in the inability to compare laboratory reported data with the numeric criteria. Without adopting the proposed amendments provided in Section V, *infra*, there are numerous instances where an exceedance of a numeric standard is likely yet the difference between the reported value and the numeric standard is not significant within scientific principles.

To provide a specific example, if a laboratory reports a value of 1700 µg/L (with two significant figures) for aluminum, that reported value is to be compared to the Standards using the criteria set forth in 20.6.4.900 NMAC for a hardness value of 60 mg/L as $CaCO_3$. The reported value of 1700 µg/L would be compared to the chronic aquatic life criteria for aluminum specified in the table of Section 20.6.4.900 I(2) NMAC of 1699 µg/L. The numeric criteria of 1699 µg/L contains four significant figures, and NMED would consider the water body as exceeding the chronic aquatic life criteria standard for aluminum. However, measuring aluminum using the EPA Method 200.7 or 200.8 set forth in 40 CFR Part 136 is not precise nor accurate to four significant figures. At best, the uncertainty in a measurement for aluminum using one of the two methods listed above would be 1700 µg/L ±10% or 1530 - 1870 µg/L. Numerous additional examples could be envisioned where a direct comparison between the Standards and a laboratory reported value with two or three significant figures would require subjective interpolation instead of direct evaluation of analytical data to the criteria set forth in 20.6.4.900 NMAC.

V. Conclusion

To eliminate instances that would require comparing measured water contaminants reported by a laboratory to a numeric standard with additional significant figures, I recommend the Standards include the following amendments:

1) Where the Ground and Surface Water Protection Regulations (20.6.2 NMAC) include numeric standards in 20.6.4.900 NMAC, revise the numeric criteria to two, or at most three, significant figures.

2) Include prescriptive steps in 20.6.4.900 NMAC, such as an algorithm, for how a laboratory report value with fewer significant figures than the numeric standard is to be compared. The NMMA proposed the following language to be included at the end of 20.6.4.900(I):

> Where a laboratory reported value has fewer significant figures than the associated numeric standard, the following algorithm is to be applied to evaluate compliance. Round the numeric standard to the same number of significant figures as reported by the laboratory, where values of 1-4 are rounded down, and values above 5 are rounded up to the next decimal. If a value includes 5 as the least significant figure, round the value to an even number.

These proposed amendments provide a clear, transparent process for comparing analytical data to the numeric standards. In the absence of these recommendations, the regulated community will struggle with inherent uncertainties that are created by the numerical limits set forth in the Standards.

This concludes my direct testimony in this matter.

DAVID A. GRATSON, CEAC
Senior Technical Chemist

ENVIRONMENTAL® STANDARDS

FIELDS OF COMPETENCE

- Proactive risk reduction via systematic project and program planning; development of measurement and data quality objectives, and Quality Assurance Project Plans to meet state and federal regulatory requirements.
- Analytical chemistry: theoretical and practical knowledge of quantitative and qualitative analysis, including forensic analysis.
- Field, laboratory, and chemical-process operation audits.
- Rigorous third-party data validation for organic, inorganics, and radionuclides.
- Training and management of laboratory and consulting staff.
- Development of project-specific geochemistry models and fate and transport parameters (Kd, solubility).
- Project-specific analytical requests for proposal (RFP) preparation.

CREDENTIALS

B.S., Biology, Allegheny College, 1981.

Additional coursework in Chemistry and Physics, University of Colorado – Denver

M.S., Environmental Science and Engineering, Colorado School of Mines, 1993.

Training in GoldSim System Modeling, including the Contaminant Transport Module, 2007.

Environmental Health and Safety Auditing Performance, 2008

CERTIFICATIONS AND AWARDS

Certified Environmental Analytical Chemist, 2004. National Registry of Certified Chemists.

R&D 100 Award, 1990.

PROFESSIONAL AFFILIATIONS

American Chemical Society
Association of Applied Geochemists
Geochemistry Society

SUMMARY OF EXPERIENCE

David has over 35 years of diversified experience in analytical and environmental chemistry and quality assurance. His career includes environmental analytical chemistry, energy research and development, specialty laboratory operation and management, and consulting.

Mr. Gratson expertise includes the fields of organic, inorganic, and radionuclide analysis. He has generated and performed site-specific sampling and analysis plans (SAP) for numerous legacy mining and remediation sites, including Quality Assurance Project Plans (QAPPs) using the Data Quality Objectives (DQO) process for state or federally supervised CERCLA, RCRA, and DoD sites. He has performed and/or overseen more than 800 technical and statistical reviews of project planning or project reporting documents, and 100 audits since 2000. The range of projects has included mine waste characterization and technology development, superfund investigations, hydraulic fracturing studies, emerging contaminants, and environmental technology development. He provided extensive expertise in systematic planning for projects that spanned a wide variety of industries and analytes.

Mr. Gratson has extensive experience in US EPA organic and inorganic analytical methodology and analytical data validation. He has validated data analyzed according to 40 CFR Part 136 requirements (100-1600 Series), drinking water regulations (500 Series), RCRA requirements (SW-846), and CERCLA/SARA requirements (Contract Laboratory Program [CLP] Statements of Work [SOWs]) and has overseen the validation efforts of many federal, state, and local projects. Mr. Gratson also has extensive experience in auditing field sampling and laboratory facilities to evaluate compliance with analytical protocols and QAPPs and to determine capabilities. He has performed more than 100 audits ranging from

mine waste remediation programs to bench scale research and emerging contaminant analysis.

Prior to joining Environmental Standards in 2012 Mr. Gratson provided chemistry and quality assurance consulting to the US EPA, the DOE, and private clients for a nationally affiliated environmental consulting firm. Projects included hydraulic fracturing case studies, mine waste technology characterization and treatment, superfund investigations and technology development, and environmental technology development and verification.

Mr. Gratson has worked in the energy R&D field, studying techniques for producing fuels and specialty chemicals using gasification and pyrolysis. He utilized direction mass spectrometry analysis, including MS/MS for identification of chemicals produced in laboratory and pilot-scale operations. At NASA, he managed a laboratory that provided qualitative and quantitative analysis (GC/FTIR/MS) of offgas components associated with the Space Shuttle and Navy Submarine environments.

KEY PROJECTS

- Lead multi-year phases for the Marcellus Shale Coalitions investigation of dissolved methane procedures across 22 laboratories. Co-designed numerous studies and was the primary author of study reports from each phase including the development of a new method that has undergone interlaboratory study validation and submitted to the US EPA for incorporation into SW-846.

- Developed SAP and performed sampling and oversaw data validation associated with an emerging contaminant investigation involving regional groundwater, process operations, and water treatment facility.

- Develop QA planning documents (SAP, QAPP, DQOs), lead field and laboratory audits, and oversaw data validation of data collected to evaluate pilot scale mine waste technology projects in California, Idaho, Montana, Nevada, Ohio, and South Dakota.

- Performed geochemical modeling using The Geochemists Workbench and PHREEQC to develop dissolved and mineral concentrations and speciation analysis in support of residual waste investigations. Using multi-site and temporal data identified redox and other geochemistry correlations and conditions that resulted in dissolved metals exceeding regulatory levels.

- Project Manager to the US EPA Office of Research and Development. Provide overall project management and technical support to the EPA under a technical quality assurance and statistical support contract. The contract supported three national laboratories and many disciplines (chemistry, biology, physics, and engineering research in all media). Guided the planning and assessed the operations and data related to innovative remediation, characterization, and monitoring research. Mr. Gratson conducted laboratory and field audits (surveillance and project-specific), quality assurance project plan reviews, and data validation and usability assessment. His team also provided systematic planning, including the data quality objectives process, and data analysis (statistical, decision analysis) support.

- R&D focus on sustainable engineering solutions to historic mining and smelting operations. Treatment, technology development at the bench and pilot scale was conducted with emphasis on passive treatment of mine waste streams in the Mountain West. Technology included physical, chemical and biological treatment (oxidation and/or reduction, neutralization) for improved water quality parameters including removal of arsenic, selenium, and other site-specific parameters of interest.

- A field study was conducted in northern Ohio to evaluate the efficacy of environmental dredging. Chemicals of concern included polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), inorganics (principally lead), and oil and grease. Part of the study involved the use of fluorescent labels coated onto fine grain sediments from the site. These tracers are then used to identify the movement of sediment once applied to specific locations. The characteristics of the fluorescent labels allow very low levels to be detected in the bed sediment or suspended sediment. The project also entailed the use of body burdens in macroinvertebrates and biological integrity measures as indicators of remedy

effectiveness and possibly watershed performance. Water column semi-permeable membrane devises were used in this research and deployed in the water column.

- Benchscale studies were designed and conducted evaluating the sorption of methyl mercury to quarry sand, site soil with high clay and iron oxides, and potential capping materials. A column study was conducted to determine the transfer of MeHg from the uncapped sediment and capped sediment to water and the gas phase. Anaerobic conditions were studied with lactic acid and sulfate added, along with a sulfate reducing bacterial (SRB) culture to simulate field conditions.

- Mr. Gratson and his team supported the EPA Superfund Innovative Technology Evaluation program for approximately seven years. This R&D program evaluated innovative remediation, characterization, and monitoring technology with the objectives to remove obstacles to the development and commercial use of innovative technologies; to gather reliable performance and cost information and to develop procedures and policies that encourage the use of innovative technologies at Superfund and other hazardous waste sites.

- Fort Devens Site (Superfund): Project planning, data analysis, and assessment. Site has natural high arsenic levels, with high levels (400-1000 µg/L) in the shallow groundwater associated with the site landfill. Soil, sediment, and groundwater sampling was conducted at the site to measure anions, ammonia, methane, metals including total and arsenic speciation (using XANES). .

- Mr. Gratson also managed consulting services to the EPA Environmental Technology Verification Program (ETV), and provided quality assurance and chemistry expertise. The ETV program verifies the performance of innovative technologies and accelerates the entrance of new environmental technologies into domestic and international marketplaces for all environmental media—air, water, and land.

- Mr. Gratson supported an agency in the development of national QA guidance documents used in project planning, data validation, and data usability. The Titles include: *Guidance on Environmental Data Verification and Data Validation* (QA/G-8) and *Guidance on Data Quality Indicators* (in development), *Guidance on Systematic Planning for Environmental Data Collection Using Performance and Acceptance Criteria* (QA/G-4a).

- Mr. Gratson's team supported studies aimed at evaluating the potential impact of Hydraulic Fracturing on groundwater. They supported the development of program planning approaches that incorporated conceptual site models, and regular program assessments. Mr. Gratson performed multiple field and laboratory audits where ground and surface water samples were collected at locations associated with unconventional oil and gas development. His auditing work assessed the analysis of organic, inorganic, and stable isotope measurements that were utilized for this project.

- Provided chemistry oversight for the development of an analytical program associated with Brownfields redevelopment at the BMI Complex for the Nevada Department of Environmental Protection. This required investigating analytical methods for over 400 chemicals of concern including organic, inorganic and radioisotopes. He and his team reviewed quality assurance documents (sampling and analysis work plans, data validation summary reports) for compliance, accuracy, usability, and overall quality assurance. He developed agency guidance on data validation, risk usability, and electronic data reporting - see https://ndep.nv.gov/environmental-cleanup/black-mountain-industrial-bmi-complex.. Significant issues at the BMI Complex include perchlorate groundwater remediation, high uranium and arsenic in localized groundwater, high levels of chlorinated compounds such as pesticides and aromatics, weathered and/or non-aroclor source PCBs, hot spots containing dioxins and furans, hexavalent chromium, organic acids from historical use requiring HPLC analysis, and use of stable isotope analysis to understand groundwater hydrology.

- Provided geochemical consulting expertise to derive transport parameters for the Performance Assessment (PA) modeling of a

low-level radioactive waste facility in Clive Utah. A GoldSim probabilistic PA model was developed to evaluate the potential for risk associated with a depleted uranium waste repository. Mr. Gratson derived solubility and Kd parameters for the radionuclides of interest for this PA which included uranium, radium, technetium, plutonium, neptunium, and iodine.

- Mr. Gratson managed metal sequestration research conducted at Indian Head Naval Surface Warfare Center (NSWC) and Marine Corps Base Quantico (MCB Quantico). At both sites, our team demonstrated pilot scale application of biosolids and/or apatite to sequester metal contaminants (zinc, lead). The demonstration plan include pre and post-amendment sampling for chemical constituents in sediment and pore water. Post-amendment testing includes bioassays to evaluate the bioavailability and resulting reduction in toxicity from the amendments.

PUBLICATIONS

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Code of Federal Regulations
Title 40. Protection of Environment
Chapter I. Environmental Protection Agency (Refs & Annos)
Subchapter D. Water Programs
Part 136. Guidelines Establishing Test Procedures for the Analysis of Pollutants (Refs & Annos)

40 C.F.R. Pt. 136, App. C

APPENDIX C TO PART 136—DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER AND WASTES BY INDUCTIVELY COUPLED PLASMA–ATOMIC EMISSION SPECTROMETRY METHOD 200.7

Effective: June 18, 2012

Currentness

1.0 Scope and Application

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP–AES) is used to determine metals and some nonmetals in solution. This method is a consolidation of existing methods for water, wastewater, and solid wastes.[1–4] (For analysis of petroleum products see References 5 and 6, Section 16.0). This method is applicable to the following analytes:

Analyte	Chemical abstract services registry number (CASRN)
Aluminum (Al)	7429-90-5
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-2
Barium (Ba)	7440-39-3
Beryllium (Be)	7440-41-7
Boron (B)	7440-42-8
Cadmium (Cd)	7440-43-9

NMMA Exhibit 3

Calcium (Ca)	7440-70-2
Ceriuma (Cr)	7440-45-1
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Iron (Fe)	7439-89-6
Lead (Pb)	7439-92-1
Lithium (Li)	7439-93-2
Magnesium (Mg)	7439-95-4
Manganese (Mn)	7439-96-5
Mercury (Hg)	7439-97-6
Molybdenum (Mo)	7439-98-7
Nickel (Ni)	7440-02-0
Phosphorus (P)	7723-14-0
Potassium (K)	7440-09-7
Selenium (Se)	7782-49-2
Silicab (Si02)	7631-86-9
Silver (Ag)	7440-22-4

NMMA Exhibit 3

Sodium (Na)	7440-23-5
Strontium (Sr)	7440-24-6
Thallium (Tl)	7440-28-0
Tin (Sn)	7440-31-5
Titanium (Ti)	7440-32-6
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

1.2 For reference where this method is approved for use in compliance monitoring programs [e.g., Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)] consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 § 141.23 for drinking water), and the latest Federal Register announcements.

1.3 ICP–AES can be used to determine dissolved analytes in aqueous samples after suitable filtration and acid preservation. To reduce potential interferences, dissolved solids should be <0.2% (w/v) (Section 4.2).

1.4 With the exception of silver, where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, samples may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has turbidity of <1 NTU at the time of analysis. This total recoverable determination procedure is referred to as “direct analysis”. However, in the determination of some primary drinking water metal contaminants, preconcentration of the sample may be required prior to analysis in order to meet drinking water acceptance performance criteria (Sections 11.2.2 through 11.2.7).

1.5 For the determination of total recoverable analytes in aqueous and solid samples a digestion/extraction is required prior to analysis when the elements are not in solution (e.g., soils, sludges, sediments and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material 1% (w/v) should be extracted as a solid type sample.

1.6 When determining boron and silica in aqueous samples, only plastic, PTFE or quartz labware should be used from time of sample collection to completion of analysis. For accurate determination of boron in solid samples only quartz or PTFE beakers should be used during acid extraction with immediate transfer of an extract aliquot to a plastic centrifuge tube following dilution of the extract to volume. When possible, borosilicate glass should be avoided to prevent contamination of these analytes.

NMMA Exhibit 3

1.7 Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved analyte or by "direct analysis" where the sample has not been processed using the total recoverable mixed acid digestion. For this reason it is recommended that samples be digested prior to the determination of silver. The total recoverable sample digestion procedure given in this method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed aliquots should be prepared until the analysis solution contains <0.1 mg/L silver. The extraction of solid samples containing concentrations of silver >50 mg/kg should be treated in a similar manner. Also, the extraction of tin from solid samples should be prepared again using aliquots <1 g when determined sample concentrations exceed 1%.

1.8 The total recoverable sample digestion procedure given in this method will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

1.9 The total recoverable sample digestion procedure given in this method is not suitable for the determination of volatile organo-mercury compounds. However, if digestion is not required (turbidity <1 NTU), the combined concentrations of inorganic and organo-mercury in solution can be determined by "direct analysis" pneumatic nebulization provided the sample solution is adjusted to contain the same mixed acid (HNO_3 + HCl) matrix as the total recoverable calibration standards and blank solutions.

1.10 Detection limits and linear ranges for the elements will vary with the wavelength selected, the spectrometer, and the matrices. Table 1 provides estimated instrument detection limits for the listed wavelengths.[7] However, actual method detection limits and linear working ranges will be dependent on the sample matrix, instrumentation, and selected operating conditions.

1.11 Users of the method data should state the data-quality objectives prior to analysis. Users of the method must document and have on file the required initial demonstration performance data described in Section 9.2 prior to using the method for analysis.

2.0 Summary of Method

2.1 An aliquot of a well mixed, homogeneous aqueous or solid sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous sample containing undissolved material, analytes are first solubilized by gentle refluxing with nitric and hydrochloric acids. After cooling, the sample is made up to volume, is mixed and centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved analytes in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of analytes in drinking water where sample turbidity is <1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid, and then diluted to a predetermined volume and mixed before analysis.

2.2 The analysis described in this method involves multielemental determinations by ICP–AES using sequential or simultaneous instruments. The instruments measure characteristic atomic-line emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the line spectra are monitored at specific wavelengths by a photosensitive device. Photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to

compensate for variable background contribution to the determination of the analytes. Background must be measured adjacent to the analyte wavelength during analysis. Various interferences must be considered and addressed appropriately as discussed in Sections 4.0, 7.0, 9.0, 10.0, and 11.0.

3.0 Definitions

3.1 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 7.10.1).

3.2 Calibration Standard (CAL)—A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration (Section 7.9).

3.3 Dissolved Analyte—The concentration of analyte in an aqueous sample that will pass through a 0.45 μm membrane filter assembly prior to sample acidification (Section 11.1).

3.4 Field Reagent Blank (FRB)—An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment (Section 8.5).

3.5 Instrument Detection Limit (IDL)—The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of 10 replicate measurements of the calibration blank signal at the same wavelength (Table 1.).

3.6 Instrument Performance Check (IPC) Solution—A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria (Sections 7.11 and 9.3.4).

3.7 Internal Standard—Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component (Section 11.5).

3.8 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 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.9 Laboratory Fortified Blank (LFB)—An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements (Sections 7.10.3 and 9.3.2).

3.10 Laboratory Fortified Sample Matrix (LFM)—An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations (Section 9.4).

3.11 Laboratory Reagent Blank (LRB)—An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus (Sections 7.10.2 and 9.3.1).

3.12 Linear Dynamic Range (LDR)—The concentration range over which the instrument response to an analyte is linear (Section 9.2.2).

3.13 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 9.2.4 and Table 4.).

3.14 Plasma Solution—A solution that is used to determine the optimum height above the work coil for viewing the plasma (Sections 7.15 and 10.2.3).

3.15 Quality Control Sample (QCS)—A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance (Sections 7.12 and 9.2.3).

3.16 Solid Sample—For the purpose of this method, a sample taken from material classified as soil, sediment or sludge.

3.17 Spectral Interference Check (SIC) Solution—A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting known interelement spectral interferences with respect to a defined set of method criteria (Sections 7.13, 7.14 and 9.3.5).

3.18 Standard Addition—The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration (Sections 9.5.1 and 11.5).

3.19 Stock Standard Solution—A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source (Section 7.8).

3.20 Total Recoverable Analyte—The concentration of analyte determined either by “direct analysis” of an unfiltered acid preserved drinking water sample with turbidity of <1 NTU (Section 11.2.1), or by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method (Sections 11.2 and 11.3).

3.21 Water Sample—For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm runoff, industrial or domestic wastewater.

4.0 Interferences

4.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

4.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurement(s) adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate not only when alternate wavelengths are desirable because of severe spectral interference, but also will show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by the measured emission on one side or the other. The location(s) selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The location(s) used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak.

4.1.2 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated for by equations that correct for interelement contributions, which involves measuring the interfering elements. Some potential on-line spectral interferences observed for the recommended wavelengths are given in Table 2. When operative and uncorrected, these interferences will produce false-positive determinations and be reported as analyte concentrations. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature that were observed with a single instrument having a working resolution of 0.035 nm are listed. More extensive information on interferant effects at various wavelengths and resolutions is available in Boumans' Tables.[8] Users may apply interelement correction factors determined on their instruments within tested concentration ranges to compensate (off-line or on-line) for the effects of interfering elements.

4.1.3 When interelement corrections are applied, there is a need to verify their accuracy by analyzing spectral interference check solutions as described in Section 7.13. Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating plus the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.[7,8]

4.1.4 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths given in Table 1, the analyst is required to determine and document for each wavelength the effect from the known interferences given in Table 2, and to utilize a computer routine for their automatic correction on all analyses. To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for their automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the user must determine and document both the on-line and off-line spectral interference effect from all method analytes and provide for their automatic correction on all analyses. Tests to determine the spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient, however, for analytes such as iron that may be found at high concentration a more appropriate test would be to use a concentration near the upper LDR limit. See Section 10.4 for required spectral interference test criteria.

4.1.5 When interelement corrections are not used, either on-going SIC solutions (Section 7.14) must be analyzed to verify the absence of interelement spectral interference or a computer software routine must be employed for comparing the

determinative data to limits files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, greater than the analyte IDL, or false negative analyte concentration, less than the 99% lower control limit of the calibration blank. When the interference accounts for 10% or more of the analyte concentration, either an alternate wavelength free of interference or another approved test procedure must be used to complete the analysis. For example, the copper peak at 213.853 nm could be mistaken for the zinc peak at 213.856 nm in solutions with high copper and low zinc concentrations. For this example, a spectral scan in the 213.8 nm region would not reveal the misidentification because a single peak near the zinc location would be observed. The possibility of this misidentification of copper for the zinc peak at 213.856 nm can be identified by measuring the copper at another emission line, e.g., 324.754 nm. Users should be aware that, depending upon the instrumental resolution, alternate wavelengths with adequate sensitivity and freedom from interference may not be available for all matrices. In these circumstances the analyte must be determined using another approved test procedure.

4.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by such means as a high-solids nebulizer, diluting the sample, using a peristaltic pump, or using an appropriate internal standard element. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. This problem can be controlled by a high-solids nebulizer, wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Also, it has been reported that better control of the argon flow rates, especially for the nebulizer, improves instrument stability and precision; this is accomplished with the use of mass flow controllers.

4.3 Chemical interferences include molecular-compound formation, ionization effects, and solute-vaporization effects. Normally, these effects are not significant with the ICP–AES technique. If observed, they can be minimized by careful selection of operating conditions (such as incident power and observation height), by buffering of the sample, by matrix matching, and by standard-addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.4 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples (Section 7.10.4). The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements corresponding to either their LDR or a concentration ten times those usually encountered. The aspiration time should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit, should be noted. Until the required rinse time is established, this method requires a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be re-analyzed after a long rinse period.

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method.[9–12] A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Specifically, 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 safety glasses or a shield for eye protection, protective clothing and observe proper mixing when working with these reagents.

5.2 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.

5.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease causative agents.

5.4 The inductively coupled plasma should only be viewed with proper eye protection from the ultraviolet emissions.

5.5 It is the responsibility of the user of this method to comply with relevant disposal and waste regulations. For guidance see Sections 14.0 and 15.0.

6.0 Equipment and Supplies

6.1 Inductively coupled plasma emission spectrometer:

6.1.1 Computer-controlled emission spectrometer with background-correction capability.

The spectrometer must be capable of meeting and complying with the requirements described and referenced in Section 2.2.

6.1.2 Radio-frequency generator compliant with FCC regulations.

6.1.3 Argon gas supply—High purity grade (99.99%). When analyses are conducted frequently, liquid argon is more economical and requires less frequent replacement of tanks than compressed argon in conventional cylinders.

6.1.4 A variable speed peristaltic pump is required to deliver both standard and sample solutions to the nebulizer.

6.1.5 (Optional) Mass flow controllers to regulate the argon flow rates, especially the aerosol transport gas, are highly recommended. Their use will provide more exacting control of reproducible plasma conditions.

6.2 Analytical balance, with capability to measure to 0.1 mg, for use in weighing solids, for preparing standards, and for determining dissolved solids in digests or extracts.

6.3 A temperature adjustable hot plate capable of maintaining a temperature of 95 °C.

6.4 (Optional) A temperature adjustable block digester capable of maintaining a temperature of 95 °C and equipped with 250 mL constricted digestion tubes.

6.5 (Optional) A steel cabinet centrifuge with guard bowl, electric timer and brake.

6.6 A gravity convection drying oven with thermostatic control capable of maintaining 180 °C ± 5 °C.

6.7 (Optional) An air displacement pipetter capable of delivering volumes ranging from 0.1–2500 µL with an assortment of high quality disposable pipet tips.

6.8 Mortar and pestle, ceramic or nonmetallic material.

6.9 Polypropylene sieve, 5–mesh (4 mm opening).

6.10 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 designated for trace element sample handling must be used. Sample containers can introduce positive and negative errors in the determination of trace elements by contributing contaminants through surface desorption or leaching, or depleting element concentrations through adsorption processes. All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. Several procedures found to provide clean labware include washing with a detergent solution, rinsing with tap water, soaking for four hours or more in 20% (v/v) nitric acid or a mixture of HNO_3 and HCl (1+2+9), rinsing with reagent water and storing clean.[23] Chromic acid cleaning solutions must be avoided because chromium is an analyte.

6.10.1 Glassware—Volumetric flasks, graduated cylinders, funnels and centrifuge tubes (glass and/or metal-free plastic).

6.10.2 Assorted calibrated pipettes.

6.10.3 Conical Phillips beakers (Corning 1080–250 or equivalent), 250 mL with 50 mm watch glasses.

6.10.4 Griffin beakers, 250 mL with 75 mm watch glasses and (optional) 75 mm ribbed watch glasses.

6.10.5 (Optional) PTFE and/or quartz Griffin beakers, 250 mL with PTFE covers.

6.10.6 Evaporating dishes or high-form crucibles, porcelain, 100 mL capacity.

6.10.7 Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125 mL to 1 L capacities.

6.10.8 One-piece stem FEP wash bottle with screw closure, 125 mL capacity.

7.0 Reagents and Standards

7.1 Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society specifications[13] should be used whenever possible. If the purity of a reagent is in question, analyze for contamination. All acids used for this method must be of ultra high-purity grade or equivalent. Suitable acids are available from a number of manufacturers. Redistilled acids prepared by sub-boiling distillation are acceptable.

7.2 Hydrochloric acid, concentrated (sp.gr. 1.19)—HCl.

7.2.1 Hydrochloric acid (1+1)—Add 500 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

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

7.2.3 Hydrochloric acid (1+20)—Add 10 mL concentrated HCl to 200 mL reagent water.

7.3 Nitric acid, concentrated (sp.gr. 1.41)—HNO_3.

7.3.1 Nitric acid (1+1)—Add 500 mL concentrated HNO_3 to 400 mL reagent water and dilute to 1 L.

7.3.2 Nitric acid (1+2)—Add 100 mL concentrated HNO_3 to 200 mL reagent water.

7.3.3 Nitric acid (1+5)—Add 50 mL concentrated HNO_3 to 250 mL reagent water.

7.3.4 Nitric acid (1+9)—Add 10 mL concentrated HNO_3 to 90 mL reagent water.

7.4 Reagent water. All references to water in this method refer to ASTM Type I grade water.[14]

7.5 Ammonium hydroxide, concentrated (sp.gr. 0.902).

7.6 Tartaric acid, ACS reagent grade.

7.7 Hydrogen peroxide, 50%, stabilized certified reagent grade.

7.8 Standard Stock Solutions—Stock standards may be purchased or prepared from ultra-high purity grade chemicals (99.99–99.999% pure). All compounds must be dried for one hour at 105 °C, unless otherwise specified. It is recommended that stock solutions be stored in FEP bottles. Replace stock standards when succeeding dilutions for preparation of calibration standards cannot be verified.

CAUTION: Many of these chemicals are extremely toxic if inhaled or swallowed (Section 5.1). Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow for 1 L quantities, but for the purpose of pollution prevention, the analyst is encouraged to prepare smaller quantities when possible. Concentrations are calculated based upon the weight of the pure element or upon the weight of the compound multiplied by the fraction of the analyte in the compound

From pure element,

$$\text{Concentration} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

From pure compound,

$$\text{Concentration} = \frac{\text{weight (mg)} \times \text{gravimetric factor}}{\text{volume (L)}}$$

where: gravimetric factor = the weight fraction of the analyte in the compound

7.8.1 Aluminum solution, stock, 1 mL = 1000 µg Al: Dissolve 1.000 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4.0 mL of (1+1) HCl and 1 mL of concentrated HNO_3 in a beaker. Warm beaker slowly to effect solution. When dissolution is complete, transfer solution quantitatively to a 1 L flask, add an additional 10.0 mL of (1+1) HCl and dilute to volume with reagent water.

7.8.2 Antimony solution, stock, 1 mL = 1000 µg Sb: Dissolve 1.000 g of antimony powder, weighed accurately to at least four significant figures, in 20.0 mL (1+1) HNO_3 and 10.0 mL concentrated HCl. Add 100 mL reagent water and 1.50 g tartaric acid. Warm solution slightly to effect complete dissolution. Cool solution and add reagent water to volume in a 1 L volumetric flask.

7.8.3 Arsenic solution, stock, 1 mL = 1000 µg As: Dissolve 1.320 g of As_2O_3 (As fraction = 0.7574), weighed accurately to at least four significant figures, in 100 mL of reagent water containing 10.0 mL concentrated NH_4OH. Warm the solution gently to effect dissolution. Acidify the solution with 20.0 mL concentrated HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.4 Barium solution, stock, 1 mL = 1000 µg Ba: Dissolve 1.437 g $BaCO_3$ (Ba fraction = 0.6960), weighed accurately to at least four significant figures, in 150 mL (1+2) HNO_3 with heating and stirring to degas and dissolve compound. Let solution cool and dilute with reagent water in 1 L volumetric flask.

7.8.5 Beryllium solution, stock, 1 mL = 1000 µg Be: DO NOT DRY. Dissolve 19.66 g $BeSO_4 \cdot 4H_2O$ (Be fraction = 0.0509), weighed accurately to at least four significant figures, in reagent water, add 10.0 mL concentrated HNO_3, and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.6 Boron solution, stock, 1 mL = 1000 µg B: DO NOT DRY. Dissolve 5.716 g anhydrous H_3BO_3 (B fraction = 0.1749), weighed accurately to at least four significant figures, in reagent water and dilute in a 1 L volumetric flask with reagent water. Transfer immediately after mixing to a clean FEP bottle to minimize any leaching of boron from the glass volumetric

container. Use of a nonglass volumetric flask is recommended to avoid boron contamination from glassware.

7.8.7 Cadmium solution, stock, 1 mL = 1000 µg Cd: Dissolve 1.000 g Cd metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1 L volumetric flask.

7.8.8 Calcium solution, stock, 1 mL = 1000 µg Ca: Suspend 2.498 g $CaCO_3$ (Ca fraction = 0.4005), dried at 180 °C for one hour before weighing, weighed accurately to at least four significant figures, in reagent water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.9 Cerium solution, stock, 1 mL = 1000 µg Ce: Slurry 1.228 g CeO_2 (Ce fraction = 0.8141), weighed accurately to at least four significant figures, in 100 mL concentrated HNO_3 and evaporate to dryness. Slurry the residue in 20 mL H_2O, add 50 mL concentrated HNO_3, with heat and stirring add 60 mL 50% H_2O_2 dropwise in 1 mL increments allowing periods of stirring between the 1 mL additions. Boil off excess H_2O_2 before diluting to volume in a 1 L volumetric flask with reagent water.

7.8.10 Chromium solution, stock, 1 mL = 1000 µg Cr: Dissolve 1.923 g CrO_3 (Cr fraction = 0.5200), weighed accurately to at least four significant figures, in 120 mL (1+5) HNO_3. When solution is complete, dilute to volume in a 1 L volumetric flask with reagent water.

7.8.11 Cobalt solution, stock, 1 mL = 1000 µg Co: Dissolve 1.000 g Co metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50.0 mL (1+1) HNO_3. Let solution cool and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.12 Copper solution, stock, 1 mL = 1000 µg Cu: Dissolve 1.000 g Cu metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50.0 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute in a 1 L volumetric flask with reagent water.

7.8.13 Iron solution, stock, 1 mL = 1000 µg Fe: Dissolve 1.000 g Fe metal, acid cleaned with (1+1) HCl, weighed accurately to four significant figures, in 100 mL (1+1) HCl with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1 L volumetric flask.

7.8.14 Lead solution, stock, 1 mL = 1000 µg Pb: Dissolve 1.599 g $Pb(NO_3)_2$ (Pb fraction = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1+1) HNO_3. Add 20.0 mL (1+1) HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.15 Lithium solution, stock, 1 mL = 1000 µg Li: Dissolve 5.324 g Li_2CO_3 (Li fraction = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1+1) HCl and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.16 Magnesium solution, stock, 1 mL = 1000 µg Mg: Dissolve 1.000 g cleanly polished Mg ribbon, accurately weighed to at least four significant figures, in slowly added 5.0 mL (1+1) HCl (CAUTION: reaction is vigorous). Add 20.0 mL (1+1) HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

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7.8.17 Manganese solution, stock, 1 mL = 1000 µg Mn: Dissolve 1.000 g of manganese metal, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.18 Mercury solution, stock, 1 mL = 1000 µg Hg: DO NOT DRY. CAUTION: highly toxic element. Dissolve 1.354 g $HgCl_2$ (Hg fraction = 0.7388) in reagent water. Add 50.0 mL concentrated HNO_3 and dilute to volume in 1 L volumetric flask with reagent water.

7.8.19 Molybdenum solution, stock, 1 mL = 1000 µg Mo: Dissolve 1.500 g MoO_3 (Mo fraction = 0.6666), weighed accurately to at least four significant figures, in a mixture of 100 mL reagent water and 10.0 mL concentrated NH_4OH, heating to effect dissolution. Let solution cool and dilute with reagent water in a 1 L volumetric flask.

7.8.20 Nickel solution, stock, 1 mL = 1000 µg Ni: Dissolve 1.000 g of nickel metal, weighed accurately to at least four significant figures, in 20.0 mL hot concentrated HNO_3, cool, and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.21 Phosphorus solution, stock, 1 mL = 1000 µg P: Dissolve 3.745 g $NH_4H_2PO_4$ (P fraction = 0.2696), weighed accurately to at least four significant figures, in 200 mL reagent water and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.22 Potassium solution, stock, 1 mL = 1000 µg K: Dissolve 1.907 g KCl (K fraction = 0.5244) dried at 110 °C, weighed accurately to at least four significant figures, in reagent water, add 20 mL (1+1) HCl and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.23 Selenium solution, stock, 1 mL = 1000 µg Se: Dissolve 1.405 g SeO_2 (Se fraction = 0.7116), weighed accurately to at least four significant figures, in 200 mL reagent water and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.24 Silica solution, stock, 1 mL = 1000 µg SiO_2: DO NOT DRY. Dissolve 2.964 g $(NH_4)_2SiF_6$, weighed accurately to at least four significant figures, in 200 mL (1+20) HCl with heating at 85 °C to effect dissolution. Let solution cool and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.25 Silver solution, stock, 1 mL = 1000 µg Ag: Dissolve 1.000 g Ag metal, weighed accurately to at least four significant figures, in 80 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1 L volumetric flask. Store solution in amber bottle or wrap bottle completely with aluminum foil to protect solution from light.

7.8.26 Sodium solution, stock, 1 mL = 1000 µg Na: Dissolve 2.542 g NaCl (Na fraction = 0.3934), weighed accurately to at least four significant figures, in reagent water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.27 Strontium solution, stock, 1 mL = 1000 µg Sr: Dissolve 1.685 g $SrCO_3$ (Sr fraction = 0.5935), weighed accurately to at least four significant figures, in 200 mL reagent water with dropwise addition of 100 mL (1+1) HCl. Dilute to volume in a 1 L volumetric flask with reagent water.

7.8.28 Thallium solution, stock, 1 mL = 1000 µg Tl: Dissolve 1.303 g $TlNO_3$ (Tl fraction = 0.7672), weighed accurately to at

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least four significant figures, in reagent water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.29 Tin solution, stock, 1 mL = 1000 µg Sn: Dissolve 1.000 g Sn shot, weighed accurately to at least four significant figures, in an acid mixture of 10.0 mL concentrated HCl and 2.0 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool, add 200 mL concentrated HCl, and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.30 Titanium solution, stock, 1 mL = 1000 µg Ti: DO NOT DRY. Dissolve 6.138 g $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$ (Ti fraction = 0.1629), weighed accurately to at least four significant figures, in 100 mL reagent water. Dilute to volume in a 1 L volumetric flask with reagent water.

7.8.31 Vanadium solution, stock, 1 mL = 1000 µg V: Dissolve 1.000 g V metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water to volume in a 1 L volumetric flask.

7.8.32 Yttrium solution, stock 1 mL = 1000 µg Y: Dissolve 1.270 g Y_2O_3 (Y fraction = 0.7875), weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3, heating to effect dissolution. Cool and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.33 Zinc solution, stock, 1 mL = 1000 µg Zn: Dissolve 1.000 g Zn metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water to volume in a 1 L volumetric flask.

7.9 Mixed Calibration Standard Solutions—For the analysis of total recoverable digested samples prepare mixed calibration standard solutions (see Table 3) by combining appropriate volumes of the stock solutions in 500 mL volumetric flasks containing 20 mL (1+1) HNO_3 and 20 mL (1+1) HCl and dilute to volume with reagent water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. To minimize the opportunity for contamination by the containers, it is recommended to transfer the mixed-standard solutions to acid-cleaned, never-used FEP fluorocarbon (FEP) bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentrations can change on aging. Calibration standards not prepared from primary standards must be initially verified using a certified reference solution. For the recommended wavelengths listed in Table 1 some typical calibration standard combinations are given in Table 3.

Note: If the addition of silver to the recommended mixed-acid calibration standard results in an initial precipitation, add 15 mL of reagent water and warm the flask until the solution clears. For this acid combination, the silver concentration should be limited to 0.5 mg/L.

7.10 Blanks—Four types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, the laboratory reagent blank is used to assess possible contamination from the sample preparation procedure, the laboratory fortified blank is used to assess routine laboratory performance and a rinse blank is used to flush the instrument uptake system and nebulizer between standards, check solutions, and samples to reduce memory interferences.

7.10.1 The calibration blank for aqueous samples and extracts is prepared by acidifying reagent water to the same concentrations of the acids as used for the standards. The calibration blank should be stored in a FEP bottle.

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7.10.2 The laboratory reagent blank (LRB) must contain all the reagents in the same volumes as used in the processing of the samples. The LRB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

7.10.3 The laboratory fortified blank (LFB) is prepared by fortifying an aliquot of the laboratory reagent blank with all analytes to a suitable concentration using the following recommended criteria: Ag 0.1 mg/L, K 5.0 mg/L and all other analytes 0.2 mg/L or a concentration approximately 100 times their respective MDL, whichever is greater. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

7.10.4 The rinse blank is prepared by acidifying reagent water to the same concentrations of acids as used in the calibration blank and stored in a convenient manner.

7.11 Instrument Performance Check (IPC) Solution—The IPC solution is used to periodically verify instrument performance during analysis. It should be prepared in the same acid mixture as the calibration standards by combining method analytes at appropriate concentrations. Silver must be limited to <0.5 mg/L; while potassium and phosphorus because of higher MDLs and silica because of potential contamination should be at concentrations of 10 mg/L. For other analytes a concentration of 2 mg/L is recommended. The IPC solution should be prepared from the same standard stock solutions used to prepare the calibration standards and stored in an FEP bottle. Agency programs may specify or request that additional instrument performance check solutions be prepared at specified concentrations in order to meet particular program needs.

7.12 Quality Control Sample (QCS)—Analysis of a QCS is required for initial and periodic verification of calibration standards or stock standard solutions in order to verify instrument performance. The QCS must be obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards. The concentration of the analytes in the QCS solution should be 1 mg/L, except silver, which must be limited to a concentration of 0.5 mg/L for solution stability. The QCS solution should be stored in a FEP bottle and analyzed as needed to meet data-quality needs. A fresh solution should be prepared quarterly or more frequently as needed.

7.13 Spectral Interference Check (SIC) Solutions—When interelement corrections are applied, SIC solutions are needed containing concentrations of the interfering elements at levels that will provide an adequate test of the correction factors.

7.13.1 SIC solutions containing (a) 300 mg/L Fe; (b) 200 mg/L AL; (c) 50 mg/L Ba; (d) 50 mg/L Be; (e) 50 mg/L Cd; (f) 50 mg/L Ce; (g) 50 mg/L Co; (h) 50 mg/L Cr; (i) 50 mg/L Cu; (j) 50 mg/L Mn; (k) 50 mg/L Mo; (l) 50 mg/L Ni; (m) 50 mg/L Sn; (n) 50 mg/L SiO_2; (o) 50 mg/L Ti; (p) 50 mg/L Tl and (q) 50 mg/L V should be prepared in the same acid mixture as the calibration standards and stored in FEP bottles. These solutions can be used to periodically verify a partial list of the on-line (and possible off-line) interelement spectral correction factors for the recommended wavelengths given in Table 1. Other solutions could achieve the same objective as well. (Multielement SIC solutions[3] may be prepared and substituted for the single element solutions provided an analyte is not subject to interference from more than one interferant in the solution.)

Note: If wavelengths other than those recommended in Table 1 are used, other solutions different from those above (a through q) may be required.

7.13.2 For interferences from iron and aluminum, only those correction factors (positive or negative) when multiplied by 100 to calculate apparent analyte concentrations that exceed the determined analyte IDL or fall below the lower 3–sigma control limit of the calibration blank need be tested on a daily basis.

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7.13.3 For the other interfering elements, only those correction factors (positive or negative) when multiplied by 10 to calculate apparent analyte concentrations that exceed the determined analyte IDL or fall below the lower 3–sigma control limit of the calibration blank need be tested on a daily basis.

7.13.4 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution (a through q) should fall within a specific concentration range bracketing the calibration blank. This concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and dividing by 10. If after subtraction of the calibration blank the apparent analyte concentration is outside (above or below) this range, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor should be updated.

Note: The SIC solution should be analyzed more than once to confirm a change has occurred with adequate rinse time between solutions and before subsequent analysis of the calibration blank.

7.13.5 If the correction factors tested on a daily basis are found to be within the 10% criteria for five consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such (e.g., finished drinking water) that they do not contain concentrations of the interfering elements at the 10 mg/L level, daily verification is not required; however, all interelement spectral correction factors must be verified annually and updated, if necessary.

7.13.6 If the instrument does not display negative concentration values, fortify the SIC solutions with the elements of interest at 1 mg/L and test for analyte recoveries that are below 95%. In the absence of measurable analyte, over-correction could go undetected because a negative value could be reported as zero.

7.14 For instruments without interelement correction capability or when interelement corrections are not used, SIC solutions (containing similar concentrations of the major components in the samples, e.g., 10 mg/L) can serve to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the SIC solution confirms an operative interference that is 10% of the analyte concentration, the analyte must be determined using a wavelength and background correction location free of the interference or by another approved test procedure. Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests.

7.15 Plasma Solution—The plasma solution is used for determining the optimum viewing height of the plasma above the work coil prior to using the method (Section 10.2). The solution is prepared by adding a 5 mL aliquot from each of the stock standard solutions of arsenic, lead, selenium, and thallium to a mixture of 20 mL (1+1) nitric acid and 20 mL (1+1) hydrochloric acid and diluting to 500 mL with reagent water. Store in a FEP bottle.

8.0 Sample Collection, Preservation, and Storage

8.1 Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples must be tested immediately prior to aliquoting for processing or “direct analysis” to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to six months before analysis.

8.2 For the determination of the dissolved elements, the sample must be filtered through a 0.45 μm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silica are critical.) Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) nitric acid immediately following filtration to pH <2.

8.3 For the determination of total recoverable elements in aqueous samples, samples are not filtered, but acidified with (1+1) nitric acid to pH <2 (normally, 3 mL of (1+1) acid per liter of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination it is recommended that the samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for 16 hours, and then verified to be pH <2 just prior withdrawing an aliquot for processing or “direct analysis”. If for some reason such as high alkalinity the sample pH is verified to be >2, more acid must be added and the sample held for 16 hours until verified to be pH <2. See Section 8.1.

Note: When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood. See Section 5.2.

8.4 Solid samples require no preservation prior to analysis other than storage at 4 °C. There is no established holding time limitation for solid samples.

8.5 For aqueous samples, a field blank should be prepared and analyzed as required by the data user. Use the same container and acid as used in sample collection.

9.0 Quality Control

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data thus generated.

9.2 Initial Demonstration of Performance (mandatory).

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear dynamic ranges and analysis of quality control samples) and laboratory performance (determination of method detection limits) prior to analyses conducted by this method.

9.2.2 Linear dynamic range (LDR)—The upper limit of the LDR must be established for each wavelength utilized. It must be determined from a linear calibration prepared in the normal manner using the established analytical operating procedure for the instrument. The LDR should be determined by analyzing succeedingly higher standard concentrations of the analyte until the observed analyte concentration is no more than 10% below the stated concentration of the standard. Determined LDRs must be documented and kept on file. The LDR which may be used for the analysis of samples should be judged by the analyst from the resulting data. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and reanalyzed. The LDRs should be verified annually or whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would

dictate they be redetermined.

9.2.3 Quality control sample (QCS)—When beginning the use of this method, on a quarterly basis, after the preparation of stock or calibration standard solutions 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 7.12). To verify the calibration standards the determined mean concentrations from three analyses of the QCS must be within 5% of the stated values. If the calibration standard cannot be verified, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding on with the initial determination of method detection limits or continuing with on-going analyses.

9.2.4 Method detection limit (MDL)—MDLs must be established for all wavelengths utilized, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit.[15] To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

MDL = (t) x (S)

where:

t = students' t value for a 99% confidence level and a standard deviation estimate with n–1 degrees of freedom [t = 3.14 for seven replicates]

S = standard deviation of the replicate analyses

Note: If additional confirmation is desired, reanalyze the seven replicate aliquots on two more nonconsecutive days and again calculate the MDL values for each day. An average of the three MDL values for each analyte may provide for a more appropriate MDL estimate. If the relative standard deviation (RSD) from the analyses of the seven aliquots is <10%, the concentration used to determine the analyte MDL may have been inappropriately high for the determination. If so, this could result in the calculation of an unrealistically low MDL. Concurrently, determination of MDL in reagent water represents a best case situation and does not reflect possible matrix effects of real world samples. However, successful analyses of LFMs (Section 9.4) and the analyte addition test described in Section 9.5.1 can give confidence to the MDL value determined in reagent water. Typical single laboratory MDL values using this method are given in Table 4.

The MDLs must be sufficient to detect analytes at the required levels according to compliance monitoring regulation (Section 1.2). MDLs should be determined annually, when a new operator begins work or whenever, in the judgment of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

9.3 Assessing Laboratory Performance (mandatory)

9.3.1 Laboratory reagent blank (LRB)—The laboratory must analyze at least one LRB (Section 7.10.2) with each batch of 20 or fewer samples of the same matrix. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the MDL indicate laboratory or reagent contamination should be suspected. When LRB values constitute

10% or more of the analyte level determined for a sample or is 2.2 times the analyte MDL whichever is greater, fresh aliquots of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been corrected and acceptable LRB values have been obtained.

9.3.2 Laboratory fortified blank (LFB)—The laboratory must analyze at least one LFB (Section 7.10.3) with each batch of samples. Calculate accuracy as percent recovery using the following equation:

$$R = \frac{LFB - LRB}{s} \times 100$$

where:

R = percent recovery

LFB = laboratory fortified blank

LRB = laboratory reagent blank

s = concentration equivalent of analyte added to fortify the LBR solution

If the recovery of any analyte falls outside the required control limits of 85–115%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3 The laboratory must use LFB analyses data to assess laboratory performance against the required control limits of 85–115% (Section 9.3.2). When sufficient internal performance data become available (usually a minimum of 20–30 analyses), optional control limits can be developed from the mean percent recovery (x) and the standard deviation (S) of the mean percent recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = x + 3S

LOWER CONTROL LIMIT = x - 3S

The optional control limits must be equal to or better than the required control limits of 85–115%. After each five to 10 new recovery measurements, new control limits can be calculated using only the most recent 20–30 data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

9.3.4 Instrument performance check (IPC) solution—For all determinations the laboratory must analyze the IPC solution (Section 7.11) and a calibration blank immediately following daily calibration, after every 10th sample (or more frequently, if required) and at the end of the sample run. Analysis of the calibration blank should always be < the analyte IDL, but greater than the lower 3–sigma control limit of the calibration blank. Analysis of the IPC solution immediately following calibration must verify that the instrument is within 5% of calibration with a relative standard deviation <3% from replicate integrations

4. Subsequent analyses of the IPC solution must be within 10% of calibration. If the calibration cannot be verified within the specified limits, reanalyze either or both the IPC solution and the calibration blank. If the second analysis of the IPC solution or the calibration blank confirm calibration to be outside the limits, sample analysis must be discontinued, the cause determined, corrected and/or the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

9.3.5 Spectral interference check (SIC) solution—For all determinations the laboratory must periodically verify the interelement spectral interference correction routine by analyzing SIC solutions. The preparation and required periodic analysis of SIC solutions and test criteria for verifying the interelement interference correction routine are given in Section 7.13. Special cases where on-going verification is required are described in Section 7.14.

9.4 Assessing Analyte Recovery and Data Quality.

9.4.1 Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess the effect. Unless otherwise specified by the data user, laboratory or program, the following laboratory fortified matrix (LFM) procedure (Section 9.4.2) is required. Also, other tests such as the analyte addition test (Section 9.5.1) and sample dilution test (Section 9.5.2) can indicate if matrix effects are operative.

9.4.2 The laboratory must add a known amount of each analyte to a minimum of 10% of the routine samples. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis and for total recoverable determinations added prior to sample preparation. For water samples, the added analyte concentration must be the same as that used in the laboratory fortified blank (Section 7.10.3). For solid samples, however, the concentration added should be expressed as mg/kg and is calculated for a one gram aliquot by multiplying the added analyte concentration (mg/L) in solution by the conversion factor 100 (mg/L x 0.1L/0.001kg = 100, Section 12.5). (For notes on Ag, Ba, and Sn see Sections 1.7 and 1.8.) Over time, samples from all routine sample sources should be fortified.

Note: The concentration of calcium, magnesium, sodium and strontium in environmental waters, along with iron and aluminum in solids can vary greatly and are not necessarily predictable. Fortifying these analytes in routine samples at the same concentration used for the LFB may prove to be of little use in assessing data quality for these analytes. For these analytes sample dilution and reanalysis using the criteria given in Section 9.5.2 is recommended. Also, if specified by the data user, laboratory or program, samples can be fortified at higher concentrations, but even major constituents should be limited to <25 mg/L so as not to alter the sample matrix and affect the analysis.

9.4.3 Calculate the percent recovery for each analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range of 70–130% or a 3–sigma recovery range calculated from the regression equations given in Table 9.[16] Recovery calculations are not required if the concentration added is less than 30% of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

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$$R = \frac{C_s - C}{s} \times 100$$

where:

R = percent recovery

C_s = fortified sample concentration

C = sample background concentration

s = concentration equivalent of analyte added to fortify the sample

9.4.4 If the recovery of any analyte falls outside the designated LFM recovery range, and the laboratory performance for that analyte is shown to be in control (Section 9.3), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The data user should be informed that the result for that analyte in the unfortified sample is suspect due to either the heterogeneous nature of the sample or matrix effects and analysis by method of standard addition or the use of an internal standard(s) (Section 11.5) should be considered.

9.4.5 Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably. Reference materials containing high concentrations of analytes can provide additional information on the performance of the spectral interference correction routine.

9.5 Assess the possible need for the method of standard additions (MSA) or internal standard elements by the following tests. Directions for using MSA or internal standard(s) are given in Section 11.5.

9.5.1 Analyte addition test: An analyte(s) standard added to a portion of a prepared sample, or its dilution, should be recovered to within 85% to 115% of the known value. The analyte(s) addition should produce a minimum level of 20 times and a maximum of 100 times the method detection limit. If the analyte addition is <20% of the sample analyte concentration, the following dilution test should be used. If recovery of the analyte(s) is not within the specified limits, a matrix effect should be suspected, and the associated data flagged accordingly. The method of additions or the use of an appropriate internal standard element may provide more accurate data.

9.5.2 Dilution test: If the analyte concentration is sufficiently high (minimally, a factor of 50 above the instrument detection

limit in the original solution but <90% of the linear limit), an analysis of a 1 + 4 dilution should agree (after correction for the fivefold dilution) within 10% of the original determination. If not, a chemical or physical interference effect should be suspected and the associated data flagged accordingly. The method of standard additions or the use of an internal-standard element may provide more accurate data for samples failing this test.

10.0 Calibration and Standardization

10.1 Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. However, because of the difference among various makes and models of spectrometers, specific instrument operating conditions cannot be given. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a task. Operating conditions for aqueous solutions usually vary from 1100–1200 watts forward power, 15–16 mm viewing height, 15–19 L/min. argon coolant flow, 0.6–1 L/min. argon aerosol flow, 1–1.8 mL/min. sample pumping rate with a one minute preflush time and measurement time near 1 s per wavelength peak (for sequential instruments) and near 10 s per sample (for simultaneous instruments). Use of the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm (by adjusting the argon aerosol flow) has been recommended as a way to achieve repeatable interference correction factors.[17]

10.2 Prior to using this method optimize the plasma operating conditions. The following procedure is recommended for vertically configured plasmas. The purpose of plasma optimization is to provide a maximum signal-to-background ratio for the least sensitive element in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow rate greatly facilitates the procedure.

10.2.1 Ignite the plasma and select an appropriate incident rf power with minimum reflected power. Allow the instrument to become thermally stable before beginning. This usually requires at least 30 to 60 minutes of operation. While aspirating the 1000 µg/mL solution of yttrium (Section 7.8.32), follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5–20 mm above the top of the work coil.[18] Record the nebulizer gas flow rate or pressure setting for future reference.

10.2.2 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min. by aspirating a known volume calibration blank for a period of at least three minutes. Divide the spent volume by the aspiration time (in minutes) and record the uptake rate. Set the peristaltic pump to deliver the uptake rate in a steady even flow.

10.2.3 After horizontally aligning the plasma and/or optically profiling the spectrometer, use the selected instrument conditions from Sections 10.2.1 and 10.2.2, and aspirate the plasma solution (Section 7.15), containing 10 µg/mL each of As, Pb, Se and Tl. Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14–18 mm above the top of the work coil. (This region of the plasma is commonly referred to as the analytical zone.)[19] Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the largest intensity ratio for the least sensitive element of the four analytes. If more than one position provides the same ratio, select the position that provides the highest net intensity counts for the least sensitive element or accept a compromise position of the intensity ratios of all four analytes.

10.2.4 The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits and method detection limits. Refer to Tables 1 and 4 for comparison of IDLs and MDLs, respectively.

10.2.5 If either the instrument operating conditions, such as incident power and/or nebulizer gas flow rate are changed, or a

new torch injector tube having a different orifice i.d. is installed, the plasma and plasma viewing height should be reoptimized.

10.2.6 Before daily calibration and after the instrument warmup period, the nebulizer gas flow must be reset to the determined optimized flow. If a mass flow controller is being used, it should be reset to the recorded optimized flow rate. In order to maintain valid spectral interelement correction routines the nebulizer gas flow rate should be the same from day-to-day (<2% change). The change in signal intensity with a change in nebulizer gas flow rate for both “hard” (Pb 220.353 nm) and “soft” (Cu 324.754) lines is illustrated in Figure 1.

10.3 Before using the procedure (Section 11.0) to analyze samples, there must be data available documenting initial demonstration of performance. The required data and procedure is described in Section 9.2. This data must be generated using the same instrument operating conditions and calibration routine (Section 11.4) to be used for sample analysis. These documented data must be kept on file and be available for review by the data user.

10.4 After completing the initial demonstration of performance, but before analyzing samples, the laboratory must establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction and for correction of interelement spectral interference in particular are given in Section 4.1. To determine the appropriate location for background correction and to establish the interelement interference correction routine, repeated spectral scan about the analyte wavelength and repeated analyses of the single element solutions may be required. Criteria for determining an interelement spectral interference is an apparent positive or negative concentration on the analyte that is outside the 3–sigma control limits of the calibration blank for the analyte. (The upper-control limit is the analyte IDL.) Once established, the entire routine must be initially and periodically verified annually, or whenever there is a change in instrument operating conditions (Section 10.2.5). Only a portion of the correction routine must be verified more frequently or on a daily basis. Test criteria and required solutions are described in Section 7.13. Initial and periodic verification data of the routine should be kept on file. Special cases where on-going verification are required is described in Section 7.14.

11.0 Procedure

11.1 Aqueous Sample Preparation—Dissolved Analytes

11.1.1 For the determination of dissolved analytes in ground and surface waters, pipet an aliquot (20 mL) of the filtered, acid preserved sample into a 50 mL polypropylene centrifuge tube. Add an appropriate volume of (1 + 1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4 mL (1 + 1) HNO_3 to a 20 mL aliquot of sample). Cap the tube and mix. The sample is now ready for analysis (Section 1.3). Allowance for sample dilution should be made in the calculations. (If mercury is to be determined, a separate aliquot must be additionally acidified to contain 1% (v/v) HCl to match the signal response of mercury in the calibration standard and reduce memory interference effects. Section 1.9).

Note: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be treated using the procedure described in Sections 11.2.2 through 11.2.7 prior to analysis.

11.2 Aqueous Sample Preparation—Total Recoverable Analytes

11.2.1 For the “direct analysis” of total recoverable analytes in drinking water samples containing turbidity <1 NTU, treat an

unfiltered acid preserved sample aliquot using the sample preparation procedure described in Section 11.1.1 while making allowance for sample dilution in the data calculation (Section 1.2). For the determination of total recoverable analytes in all other aqueous samples or for preconcentrating drinking water samples prior to analysis follow the procedure given in Sections 11.2.2 through 11.2.7.

11.2.2 For the determination of total recoverable analytes in aqueous samples (other than drinking water with <1 NTU turbidity), transfer a 100 mL (1 mL) aliquot from a well mixed, acid preserved sample to a 250 mL Griffin beaker (Sections 1.2, 1.3, 1.6, 1.7, 1.8, and 1.9). (When necessary, smaller sample aliquot volumes may be used.)

Note: If the sample contains undissolved solids >1%, a well mixed, acid preserved aliquot containing no more than 1 g particulate material should be cautiously evaporated to near 10 mL and extracted using the acid-mixture procedure described in Sections 11.3.3 through 11.3.6.

11.2.3 Add 2 mL (1+1) nitric acid and 1.0 mL of (1+1) hydrochloric acid to the beaker containing the measured volume of sample. Place the beaker on the hot plate for solution evaporation. The hot plate should be located in a fume hood and previously adjusted to provide evaporation at a temperature of approximately but no higher than 85 °C. (See the following note.) The beaker should be covered with an elevated watch glass or other necessary steps should be taken to prevent sample contamination from the fume hood environment.

Note: For proper heating adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85 °C. (Once the beaker is covered with a watch glass the temperature of the water will rise to approximately 95 °C.)

11.2.4 Reduce the volume of the sample aliquot to about 20 mL by gentle heating at 85 °C. DO NOT BOIL. This step takes about two hours for a 100 mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL. (A spare beaker containing 20 mL of water can be used as a gauge.)

11.2.5 Cover the lip of the beaker with a watch glass to reduce additional evaporation and gently reflux the sample for 30 minutes. (Slight boiling may occur, but vigorous boiling must be avoided to prevent loss of the HCl–H_2O azeotrope.)

11.2.6 Allow the beaker to cool. Quantitatively transfer the sample solution to a 50 mL volumetric flask, make to volume with reagent water, stopper and mix.

11.2.7 Allow any undissolved material to settle overnight, or centrifuge a portion of the prepared sample until clear. (If after centrifuging or standing overnight the sample contains suspended solids that would clog the nebulizer, a portion of the sample may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.) The sample is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

11.3 Solid Sample Preparation—Total Recoverable Analytes

11.3.1 For the determination of total recoverable analytes in solid samples, mix the sample thoroughly and transfer a portion (>20 g) to tared weighing dish, weigh the sample and record the wet weight (WW). (For samples with <35% moisture a 20 g

portion is sufficient. For samples with moisture >35% a larger aliquot 50–100 g is required.) Dry the sample to a constant weight at 60 °C and record the dry weight (DW) for calculation of percent solids (Section 12.6). (The sample is dried at 60 °C to prevent the loss of mercury and other possible volatile metallic compounds, to facilitate sieving, and to ready the sample for grinding.)

11.3.2 To achieve homogeneity, sieve the dried sample using a 5–mesh polypropylene sieve and grind in a mortar and pestle. (The sieve, mortar and pestle should be cleaned between samples.) From the dried, ground material weigh accurately a representative 1.0 ± 0.01 g aliquot (W) of the sample and transfer to a 250 mL Phillips beaker for acid extraction (Sections 1.6, 1.7, 1.8, and 1.9).

11.3.3 To the beaker add 4 mL of (1+1) HNO_3 and 10 mL of (1+4) HCl. Cover the lip of the beaker with a watch glass. Place the beaker on a hot plate for reflux extraction of the analytes. The hot plate should be located in a fume hood and previously adjusted to provide a reflux temperature of approximately 95 °C. (See the following note.)

Note: For proper heating adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85 °C. (Once the beaker is covered with a watch glass the temperature of the water will rise to approximately 95 °C.) Also, a block digester capable of maintaining a temperature of 95 °C and equipped with 250 mL constricted volumetric digestion tubes may be substituted for the hot plate and conical beakers in the extraction step.

11.3.4 Heat the sample and gently reflux for 30 minutes. Very slight boiling may occur, however vigorous boiling must be avoided to prevent loss of the HCl–H_2O azeotrope. Some solution evaporation will occur (3–4 mL).

11.3.5 Allow the sample to cool and quantitatively transfer the extract to a 100 mL volumetric flask. Dilute to volume with reagent water, stopper and mix.

11.3.6 Allow the sample extract solution to stand overnight to separate insoluble material or centrifuge a portion of the sample solution until clear. (If after centrifuging or standing overnight the extract solution contains suspended solids that would clog the nebulizer, a portion of the extract solution may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.) The sample extract is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

11.4 Sample Analysis

11.4.1 Prior to daily calibration of the instrument inspect the sample introduction system including the nebulizer, torch, injector tube and uptake tubing for salt deposits, dirt and debris that would restrict solution flow and affect instrument performance. Clean the system when needed or on a daily basis.

11.4.2 Configure the instrument system to the selected power and operating conditions as determined in Sections 10.1 and 10.2.

11.4.3 The instrument must be allowed to become thermally stable before calibration and analyses. This usually requires at least 30 to 60 minutes of operation. After instrument warmup, complete any required optical profiling or alignment particular

to the instrument.

11.4.4 For initial and daily operation calibrate the instrument according to the instrument manufacturer's recommended procedures, using mixed calibration standard solutions (Section 7.9) and the calibration blank (Section 7.10.1). A peristaltic pump must be used to introduce all solutions to the nebulizer. To allow equilibrium to be reached in the plasma, aspirate all solutions for 30 seconds after reaching the plasma before beginning integration of the background corrected signal to accumulate data. When possible, use the average value of replicate integration periods of the signal to be correlated to the analyte concentration. Flush the system with the rinse blank (Section 7.10.4) for a minimum of 60 seconds (Section 4.4) between each standard. The calibration line should consist of a minimum of a calibration blank and a high standard. Replicates of the blank and highest standard provide an optimal distribution of calibration standards to minimize the confidence band for a straight-line calibration in a response region with uniform variance.[20]

11.4.5 After completion of the initial requirements of this method (Sections 10.3 and 10.4), samples should be analyzed in the same operational manner used in the calibration routine with the rinse blank also being used between all sample solutions, LFBs, LFMs, and check solutions (Section 7.10.4).

11.4.6 During the analysis of samples, the laboratory must comply with the required quality control described in Sections 9.3 and 9.4. Only for the determination of dissolved analytes or the "direct analysis" of drinking water with turbidity of <1 NTU is the sample digestion step of the LRB, LFB, and LFM not required.

11.4.7 Determined sample analyte concentrations that are 90% or more of the upper limit of the analyte LDR must be diluted with reagent water that has been acidified in the same manner as calibration blank and reanalyzed (see Section 11.4.8). Also, for the interelement spectral interference correction routines to remain valid during sample analysis, the interferant concentration must not exceed its LDR. If the interferant LDR is exceeded, sample dilution with acidified reagent water and reanalysis is required. In these circumstances analyte detection limits are raised and determination by another approved test procedure that is either more sensitive and/or interference free is recommended.

11.4.8 When it is necessary to assess an operative matrix interference (e.g., signal reduction due to high dissolved solids), the tests described in Section 9.5 are recommended.

11.4.9 Report data as directed in Section 12.0.

11.5 If the method of standard additions (MSA) is used, standards are added at one or more levels to portions of a prepared sample. This technique[21] compensates for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single-addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated by the following:

$$\text{Sample Conc. (mg/L or mg/kg)} = \frac{S_2 \times V_1 \times C}{(S_1 - S_2) \times V_2}$$

where:

C = Concentration of the standard solution (mg/L)

S_1 = Signal for fortified aliquot

S_2 = Signal for unfortified aliquot

V_1 = Volume of the standard addition (L)

V_2 = Volume of the sample aliquot (L) used for MSA

For more than one fortified portion of the prepared sample, linear regression analysis can be applied using a computer or calculator program to obtain the concentration of the sample solution. An alternative to using the method of standard additions is use of the internal standard technique by adding one or more elements (not in the samples and verified not to cause an uncorrected interelement spectral interference) at the same concentration (which is sufficient for optimum precision) to the prepared samples (blanks and standards) that are affected the same as the analytes by the sample matrix. Use the ratio of analyte signal to the internal standard signal for calibration and quantitation.

12.0 Data Analysis and Calculations

12.1 Sample data should be reported in units of mg/L for aqueous samples and mg/kg dry weight for solid samples.

12.2 For dissolved aqueous analytes (Section 11.1) report the data generated directly from the instrument with allowance for sample dilution. Do not report analyte concentrations below the IDL.

12.3 For total recoverable aqueous analytes (Section 11.2), multiply solution analyte concentrations by the dilution factor 0.5, when 100 mL aliquot is used to produce the 50 mL final solution, and report data as instructed in Section 12.4. If a different aliquot volume other than 100 mL is used for sample preparation, adjust the dilution factor accordingly. Also, account for any additional dilution of the prepared sample solution needed to complete the determination of analytes exceeding 90% or more of the LDR upper limit. Do not report data below the determined analyte MDL concentration or below an adjusted detection limit reflecting smaller sample aliquots used in processing or additional dilutions required to complete the analysis.

12.4 For analytes with MDLs <0.01 mg/L, round the data values to the thousandth place and report analyte concentrations up to three significant figures. For analytes with MDLs <0.01 mg/L round the data values to the 100th place and report analyte concentrations up to three significant figures. Extract concentrations for solids data should be rounded in a similar manner before calculations in Section 12.5 are performed.

12.5 For total recoverable analytes in solid samples (Section 11.3), round the solution analyte concentrations (mg/L) as instructed in Section 12.4. Report the data up to three significant figures as mg/kg dry-weight basis unless specified otherwise by the program or data user. Calculate the concentration using the equation below:

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$$\text{Sample Conc. (mg/kg) dry} - \text{weight basis} = \frac{C \times V \times D}{W}$$

where:

C = Concentration in extract (mg/L)

V = Volume of extract (L, 100 mL = 0.1L)

D = Dilution factor (undiluted = 1)

W = Weight of sample aliquot extracted (g x 0.001 = kg)

Do not report analyte data below the estimated solids MDL or an adjusted MDL because of additional dilutions required to complete the analysis.

12.6 To report percent solids in solid samples (Section 11.3) calculate as follows:

$$\%\ \text{solids (S)} = \frac{DW}{WW} \times 100$$

where:

DW = Sample weight (g) dried at 60 °C

WW = Sample weight (g) before drying

Note: If the data user, program or laboratory requires that the reported percent solids be determined by drying at 105 °C, repeat the procedure given in Section 11.3 using a separate portion (>20 g) of the sample and dry to constant weight at 103–105 °C.

12.7 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.

13.0 Method Performance

13.1 Listed in Table 4 are typical single laboratory total recoverable MDLs determined for the recommended wavelengths using simultaneous ICP–AES and the operating conditions given in Table 5. The MDLs were determined in reagent blank matrix (best case situation). PTFE beakers were used to avoid boron and silica contamination from glassware with the final dilution to 50 mL completed in polypropylene centrifuged tubes. The listed MDLs for solids are estimates and were

calculated from the aqueous MDL determinations.

13.2 Data obtained from single laboratory method testing are summarized in Table 6 for five types of water samples consisting of drinking water, surface water, ground water, and two wastewater effluents. The data presented cover all analytes except cerium and titanium. Samples were prepared using the procedure described in Section 11.2. For each matrix, five replicate aliquots were prepared, analyzed and the average of the five determinations used to define the sample background concentration of each analyte. In addition, two pairs of duplicates were fortified at different concentration levels. For each method analyte, the sample background concentration, mean percent recovery, standard deviation of the percent recovery, and relative percent difference between the duplicate fortified samples are listed in Table 6. The variance of the five replicate sample background determinations is included in the calculated standard deviation of the percent recovery when the analyte concentration in the sample was greater than the MDL. The tap and well waters were processed in Teflon and quartz beakers and diluted in polypropylene centrifuged tubes. The nonuse of borosilicate glassware is reflected in the precision and recovery data for boron and silica in those two sample types.

13.3 Data obtained from single laboratory method testing are summarized in Table 7 for three solid samples consisting of EPA 884 Hazardous Soil, SRM 1645 River Sediment, and EPA 286 Electroplating Sludge. Samples were prepared using the procedure described in Section 11.3. For each method analyte, the sample background concentration, mean percent recovery of the fortified additions, the standard deviation of the percent recovery, and relative percent difference between duplicate additions were determined as described in Section 13.2. Data presented are for all analytes except cerium, silica, and titanium. Limited comparative data to other methods and SRM materials are presented in Reference 23 of Section 16.0.

13.4 Performance data for aqueous solutions independent of sample preparation from a multilaboratory study are provided in Table 8.[22]

13.5 Listed in Table 9 are regression equations for precision and bias for 25 analytes abstracted from EPA Method Study 27, a multilaboratory validation study of Method 200.7.[1] These equations were developed from data received from 12 laboratories using the total recoverable sample preparation procedure on reagent water, drinking water, surface water and three industrial effluents. For a complete review and description of the study, see Reference 16 of Section 16.0.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous 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 (e.g., Section 7.8). When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable 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.

15.0 Waste Management

15.1 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 the Section 14.2.

16.0 References

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17.0 Tables, Diagrams, Flowcharts, and Validation Data

Table 1—Wavelengths, Estimated Instrument Detection Limits, and Recommended Calibration

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Analyte	Wavelength[a] (nm)	Estimated detection limit[b] (μg/L)	Calibrate[c] to (mg/L)
Aluminum	308.215	45	10
Antimony	206.833	32	5
Arsenic	193.759	53	10
Barium	493.409	2.3	1
Beryllium	313.042	0.27	1
Boron	249.678	5.7	1
Cadmium	226.502	3.4	2
Calcium	315.887	30	10
Cerium	413.765	48	2
Chromium	205.552	6.1	5
Cobalt	228.616	7.0	2
Copper	324.754	5.4	2
Iron	259.940	6.2	10
Lead	220.353	42	10
Lithium	670.784	[d] 3.7	5
Magnesium	279.079	30	10

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Manganese	257.610	1.4	2
Mercury	194.227	2.5	2
Molybdenum	203.844	12	10
Nickel	231.604	15	2
Phosphorus	214.914	76	10
Potassium	766.491	[e] 700	20
Selenium	196.090	75	5
Silica (SiO_2)	251.611	[d] 26 (SiO_2)	10
Silver	328.068	7.0	0.5
Sodium	588.995	29	10
Strontium	421.552	0.77	1
Thallium	190.864	40	5
Tin	189.980	25	4
Titanium	334.941	3.8	10
Vanadium	292.402	7.5	2
Zinc	213.856	1.8	5

TABLE 2—On-Line Method Interelement Spectral Interferances Arising From Interferants at the 100 mg/L Level

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Analyte	Wavelength (nm)	Interferant *
Ag	328.068	Ce, Ti, Mn
Al	308.215	V, Mo, Ce, Mn
As	193.759	V, Al, Co, Fe, Ni
B	249.678	None
Ba	493.409	None
Be	313.042	V, Ce
Ca	315.887	Co, Mo, Ce
Cd	226.502	Ni, Ti, Fe, Ce
Ce	413.765	None
Co	228.616	Ti, Ba, Cd, Ni, Cr, Mo, Ce
Cr	205.552	Be, Mo, Ni
Cu	324.754	Mo, Ti
Fe	259.940	None
Hg	194.227	V, Mo
K	766.491	None
Li	670.784	None
Mg	279.079	Ce

NMMA Exhibit 3

Mn	257.610	Ce
Mo	203.844	Ce
Na	588.995	None
Ni	231.604	Co, Tl
P	214.914	Cu, Mo
Pb	220.353	Co, Al, Ce, Cu, Ni, Ti, Fe
Sb	206.833	Cr, Mo, Sn, Ti, Ce, Fe
Se	196.099	Fe
SiO_2	251.611	None
Sn	189.980	Mo, Ti, Fe, Mn, Si
Sr	421.552	None
Tl	190.864	Ti, Mo, Co, Ce, Al, V, Mn
Ti	334.941	None
V	292.402	Mo, Ti, Cr, Fe, Ce
Zn	213.856	Ni, Cu, Fe

TABLE 3—Mixed Standard Solutions

Solution	Analytes

NMMA Exhibit 3

I	Ag, As, B, Ba, Ca, Cd, Cu, Mn, Sb, and Se
II	K, Li, Mo, Na, Sr, and Ti
III	Co, P, V, and Ce
IV	Al, Cr, Hg, SiO_2, Sn, and Zn
V	Be, Fe, Mg, Ni, Pb, and Tl

TABLE 4—Total Recoverable Method Detection Limits (MDL)

Analyte	MDLs	
	Aqueous, mg/L[1]	Solids, mg/kg[2]
Ag	0.002	0.3
Al	0.02	3
As	0.008	2
B	0.003	—
Ba	0.001	0.2
Be	0.0003	0.1
Ca	0.01	2
Cd	0.001	0.2
Ce	0.02	3
Co	0.002	0.4

Cr	0.004	0.8
Cu	0.003	0.5
Fe	* 0.03	6
Hg	0.007	2
K	0.3	60
Li	0.001	0.2
Mg	0.02	3
Mn	0.001	0.2
Mo	0.004	1
Na	0.03	6
Ni	0.005	1
P	0.06	12
Pb	0.01	2
Sb	0.008	2
Se	0.02	5
SiO_2	0.02	—
Sn	0.007	2
Sr	0.0003	0.1

Tl	0.001	0.2
Ti	0.02	3
V	0.003	1
Zn	0.002	0.3

— Boron not reported because of glassware contamination. Silica not determined in solid samples.

TABLE 5—Inductively Coupled Plasma Instrument Operating Conditions

Incident rf power	1100 watts
Reflected rf power	<5 watts
Viewing height above work coil	15 mm
Injector tube orifice i.d.	1 mm
Argon supply	liquid argon
Argon pressure	40 psi
Coolant argon flow rate	19 L/min.
Aerosol carrier argon flow rate	620 mL/min.
Auxiliary (plasma) argon flow rate	300 mL/min.
Sample uptake rate controlled to	1.2 mL/min.

NMMA Exhibit 3

Table 6—Precision and Recovery Data in Aqueous Matrices

Analyte	Sample conc.	Low spike	Average	S (R)	RPD	High spike	Average	S (R)	RPD
	mg/L	mg/L	recovery R(%)			mg/L	recovery R (%)		
Tap Water									
Ag	<0.002	0.05	95	0.7	2.1	0.2	96	0.0	0.0
Al	0.185	0.05	98	8.8	1.7	0.2	105	3.0	3.1
As	<0.008	0.05	108	1.4	3.7	0.2	101	0.7	2.0
B	0.023	0.1	98	0.2	0.0	0.4	98	0.2	0.5
Ba	0.042	0.05	102	1.6	2.2	0.2	98	0.4	0.8
Be	<0.0003	0.01	100	0.0	0.0	0.1	99	0.0	0.0
Ca	35.2	5.0	101	8.8	1.7	20.0	103	2.0	0.9
Cd	<0.001	0.01	105	3.5	9.5	0.1	98	0.0	0.0
Co	<0.002	0.02	100	0.0	0.0	0.2	99	0.5	1.5
Cr	<0.004	0.01	110	0.0	0.0	0.1	102	0.0	0.0
Cu	<0.003	0.02	103	1.8	4.9	0.2	101	1.2	3.5
Fe	0.008	0.1	106	1.0	1.8	0.4	105	0.3	0.5
Hg	<0.007	0.05	103	0.7	1.9	0.2	100	0.4	1.0

NMMA Exhibit 3

K	1.98	5.0	109	1.4	2.3	20.	107	0.7	1.7
Li	0.006	0.02	103	6.9	3.8	0.2	110	1.9	4.4
Mg	8.08	5.0	104	2.2	1.5	20.0	100	0.7	1.1
Mn	<0.001	0.01	100	0.0	0.0	0.1	99	0.0	0.0
Mo	<0.004	0.02	95	3.5	10.5	0.2	108	0.5	1.4
Na	10.3	5.0	99	3.0	2.0	20.0	106	1.0	1.6
Ni	<0.005	0.02	108	1.8	4.7	0.2	104	1.1	2.9
P	0.045	0.1	102	13.1	9.4	0.4	104	3.2	1.3
Pb	<0.01	0.05	95	0.7	2.1	0.2	100	0.2	0.5
Sb	<0.008	0.05	99	0.7	2.0	0.2	102	0.7	2.0
Se	<0.02	0.1	87	1.1	3.5	0.4	99	0.8	2.3
SiO_2	6.5	5.0	104	3.3	3.4	20.0	96	1.1	2.3
Sn	<0.007	0.05	103	2.1	5.8	0.2	101	1.8	5.0
Sr	0.181	0.1	102	3.3	2.1	0.4	105	0.8	1.0
Tl	<0.02	0.1	101	3.9	10.9	0.4	101	0.1	0.3
V	<0.003	0.05	101	0.7	2.0	0.2	99	0.2	0.5

NMMA Exhibit 3

Zn	0.005	0.05	101	3.7	9.0	0.2	98	0.9	2.5
Pond Water									
Ag	<0.002	0.05	92	0.0	0.0	0.2	94	0.0	0.0
Al	0.819	0.2	88	10.0	5.0	0.8	100	2.9	3.7
As	<0.008	0.05	102	0.0	0.0	0.2	98	1.4	4.1
B	0.034	0.1	111	8.9	6.9	0.4	103	2.0	0.0
Ba	0.029	0.05	96	0.9	0.0	0.2	97	0.3	0.5
Be	<0.0003	0.01	95	0.4	1.1	0.2	95	0.0	0.0
Ca	53.9	5.0	*	*	0.7	20.0	100	2.0	1.5
Cd	<0.001	0.01	107	0.0	0.0	0.1	97	0.0	0.0
Co	<0.002	0.02	100	2.7	7.5	0.2	97	0.7	2.1
Cr	<0.004	0.01	105	3.5	9.5	0.1	103	1.1	2.9
Cu	<0.003	0.02	98	2.1	4.4	0.2	100	0.5	1.5
Fe	0.875	0.2	95	8.9	2.8	0.8	97	3.2	3.6
Hg	<0.007	0.05	97	3.5	10.3	0.2	98	0.0	0.0
K	2.48	5.0	106	0.3	0.1	20.0	103	0.2	0.4
Li	<0.001	0.02	110	0.0	0.0	0.2	106	0.2	0.5

NMMA Exhibit 3

Mg	10.8	5.0	102	0.5	0.0	20.0	96	0.7	1.3
Mn	0.632	0.01	*	*	0.2	0.1	97	2.3	0.3
Mo	<0.004	0.02	105	3.5	9.5	0.2	103	0.4	1.0
Na	17.8	5.0	103	1.3	0.4	20.0	94	0.3	0.0
Ni	<0.005	0.02	96	5.6	9.1	0.2	100	0.7	1.5
P	0.196	0.1	91	14.7	0.3	0.4	108	3.9	1.3
Pb	<0.01	0.05	96	2.6	7.8	0.2	100	0.7	2.0
Sb	<0.008	0.05	102	2.8	7.8	0.2	104	0.4	1.0
Se	<0.02	0.1	104	2.1	5.8	0.4	103	1.6	4.4
SiO_2	7.83	5.0	151	1.6	1.3	20.0	117	0.4	0.6
Sn	<0.007	0.05	98	0.0	0.0	0.2	99	1.1	3.0
Sr	0.129	0.1	105	0.4	0.0	0.4	99	0.1	0.2
Tl	<0.02	0.1	103	1.1	2.9	0.4	97	1.3	3.9
V	0.003	0.05	94	0.4	0.0	0.2	98	0.1	0.0
Zn	0.006	0.05	97	1.6	1.8	0.2	94	0.4	0.0
Well Water									
Ag	<0.002	0.05	97	0.7	2.1	0.2	96	0.2	0.5

NMMA Exhibit 3

Al	0.036	0.05	107	7.6	10.1	0.2	101	1.1	0.8
As	<0.008	0.05	107	0.7	1.9	0.2	104	0.4	1.0
B	0.063	0.1	97	0.6	0.7	0.4	98	0.8	2.1
Ba	0.102	0.05	102	3.0	0.0	0.2	99	0.9	1.0
Be	<0.0003	0.01	100	0.0	0.0	0.1	100	0.0	0.0
Ca	93.8	5.0	*	*	2.1	20.0	100	4.1	0.1
Cd	0.002	0.01	90	0.0	0.0	0.1	96	0.0	0.0
Co	<0.002	0.02	94	0.4	1.1	0.2	94	0.4	1.1
Cr	<0.004	0.01	100	7.1	20.0	0.1	100	0.4	1.0
Cu	<0.005	0.02	100	1.1	0.4	0.2	96	0.5	1.5
Fe	0.042	0.1	99	2.3	1.4	0.4	97	1.4	3.3
Hg	<0.007	0.05	94	2.8	8.5	0.2	93	1.2	3.8
K	6.21	5.0	96	3.4	3.6	20.0	101	1.2	2.3
Li	0.001	0.02	100	7.6	9.5	0.2	104	1.0	1.9
Mg	24.5	5.0	95	5.6	0.3	20.0	93	1.6	1.2
Mn	2.76	0.01	*	*	0.4	0.1	*	*	0.7
Mo	<0.004	0.02	108	1	4	0.2	101	0	0

NMMA Exhibit 3

				.8	.7			.2	.5
Na	35.0	5.0	101	11.4	0.8	20.0	100	3.1	1.5
Ni	<0.005	0.02	112	1.8	4.4	0.2	96	0.2	0.5
P	0.197	0.1	95	12.7	1.9	0.4	98	3.4	0.9
Pb	<0.01	0.05	87	4.9	16.1	0.2	95	0.2	0.5
Sb	<0.008	0.05	98	2.8	8.2	0.2	99	1.4	4.0
Se	<0.02	0.1	102	0.4	1.0	0.4	94	1.1	3.4
SiO_2	13.1	5.0	93	4.8	2.8	20.0	99	0.8	0.0
Sn	<0.007	0.05	98	2.8	8.2	0.2	94	0.2	0.5
Sr	0.274	0.1	94	5.7	2.7	0.4	95	1.7	2.2
Tl	<0.02	0.1	92	0.4	1.1	0.4	95	1.1	3.2
V	<0.003	0.05	98	0.0	0.0	0.2	99	0.4	1.0
Zn	0.538	0.05	*	*	0.7	0.2	99	2.5	1.1
Sewage Treatment Effluent									
Ag	0.009	0.05	92	1.5	3.6	0.2	95	0.1	0.0
Al	1.19	0.05	*	*	0.9	0.2	113	12.4	2.1
As	<0.008	0.05	99	2.	6.	0.2	93	2.	6.

NMMA Exhibit 3

				1	1			1	5
B	0.226	0.1	217	16.3	9.5	0.4	119	13.1	20.9
Ba	0.189	0.05	90	6.8	1.7	0.2	99	1.6	0.5
Be	<0.0003	0.01	94	0.4	1.1	0.1	100	0.4	1.0
Ca	87.9	5.0	*	*	0.6	20.0	101	3.7	0.0
Cd	0.009	0.01	89	2.6	2.3	0.1	97	0.4	1.0
Co	0.016	0.02	95	3.1	0.0	0.2	93	0.4	0.5
Cr	0.128	0.01	*	*	1.5	0.1	97	2.4	2.7
Cu	0.174	0.02	98	33.1	4.7	0.2	98	3.0	1.4
Fe	1.28	0.1	*	*	2.8	0.4	111	7.0	0.6
Hg	<0.007	0.05	102	1.4	3.9	0.2	98	0.5	1.5
K	10.6	5.0	104	2.8	1.3	20.0	101	0.6	0.0
Li	0.011	0.02	103	8.5	3.2	0.2	105	0.8	0.5
Mg	22.7	5.0	100	4.4	0.0	20.0	92	1.1	0.2
Mn	0.199	0.01	*	*	2.0	0.1	104	1.9	0.3
Mo	0.125	0.02	110	21.2	6.8	0.2	102	1.3	0.9
Na	0.236	5.0	*	*	0.0	20.0	*	*	0.4

NMMA Exhibit 3

Ni	0.087	0.02	122	10.7	4.5	0.2	98	0.8	1.1
P	4.71	0.1	*	*	2.6	0.4	*	*	1.4
Pb	0.015	0.05	91	3.5	5.0	0.2	96	1.3	2.9
Sb	<0.008	0.05	97	0.7	2.1	0.2	103	1.1	2.9
Se	<0.02	0.1	108	3.9	10.0	0.4	101	2.6	7.2
SiO_2	16.7	5.0	124	4.0	0.9	20.0	108	1.1	0.8
Sn	0.016	0.05	90	3.8	0.0	0.2	95	1.0	0.0
Sr	0.515	0.1	103	6.4	0.5	0.4	96	1.6	0.2
Tl	<0.02	0.1	105	0.4	1.0	0.4	95	0.0	0.0
V	0.003	0.05	93	0.9	2.0	0.2	97	0.2	0.5
Zn	0.160	0.05	98	3.3	1.9	0.2	101	1.0	1.4
Industrial Effluent									
Ag	<0.0003	0.05	88	0.0	0.0	0.2	84	0.9	3.0
Al	0.054	0.05	88	11.7	12.2	0.2	90	3.9	8.1
As	<0.02	0.05	82	2.8	9.8	0.2	88	0.5	1.7
B	0.17	0.1	162	17.6	13.9	0.4	92	4.7	9.3

Ba	0.083	0.05	86	8.2	1.6	0.2	85	2.3	2.4
Be	<0.0006	0.01	94	0.4	1.1	0.1	82	1.4	4.9
Ca	500	5.0	*	*	2.8	20.0	*	*	2.3
Cd	0.008	0.01	85	4.7	6.1	0.1	82	1.4	4.4
Co	<0.004	0.02	93	1.8	5.4	0.2	83	0.4	1.2
Cr	0.165	0.01	*	*	4.5	0.1	106	6.6	5.6
Cu	0.095	0.02	93	23.3	0.9	0.2	95	2.7	2.8
Fe	0.315	0.1	88	16.4	1.0	0.4	99	6.5	8.0
Hg	<0.01	0.05	87	0.7	2.3	0.2	86	0.4	1.2
K	2.87	5.0	101	3.4	2.4	20.0	100	0.8	0.4
Li	0.069	0.02	103	24.7	5.6	0.2	104	2.5	2.2
Mg	6.84	5.0	87	3.1	0.0	20.0	87	0.9	1.2
Mn	0.141	0.01	*	*	1.2	0.1	89	6.6	4.8
Mo	1.27	0.02	*	*	0.0	0.2	100	15.0	2.7
Na	1500	5.0	*	*	2.7	20.0	*	*	2.0
Ni	0.014	0.02	98	4.4	3.0	0.2	87	0.5	1.1

NMMA Exhibit 3

P	0.326	0.1	105	16.0	4.7	0.4	97	3.9	1.4
Pb	0.251	0.05	80	19.9	1.4	0.2	88	5.0	0.9
Sb	2.81	0.05	*	*	0.4	0.2	*	*	2.0
Se	0.021	0.1	106	2.6	3.2	0.4	105	1.9	4.6
SiO_2	6.83	5.0	99	6.8	1.7	20.0	100	2.2	3.0
Sn	<0.01	0.05	87	0.7	2.3	0.2	86	0.4	1.2
Sr	6.54	0.1	*	*	2.0	0.4	*	*	2.7
Tl	<0.03	0.1	87	1.8	5.8	0.4	84	1.1	3.6
V	<0.005	0.05	90	1.4	4.4	0.2	84	1.1	3.6
Zn	0.024	0.05	89	6.0	4.4	0.2	91	3.5	8.9

S (R) Standard deviation of percent recovery.

RPD Relative percent difference between duplicate spike determinations.

< Sample concentration below established method detection limit.

Table 7—Precision and Recovery Data in Solid Matrices

Analyte	Sample conc.	Low + spike	Average	S (R)	RPD	High + spike	Average	S (R)	RPD
	mg/kg								
	mg/kg								

	recovery R (%)								
	mg/kg								
	recovery R (%)								
EPA Hazardous Soil #884									
Ag	1.1	20	98	0.7	1.0	100	96	0.2	0.6
Al	5080	20	*	*	7.2	100	*	*	5.4
As	5.7	20	95	5.4	10.6	100	96	1.4	3.6
B	20.4	100	93	2.7	5.3	400	100	2.1	5.5
Ba	111	20	98	71.4	22.2	100	97	10.0	1.0
Be	0.66	20	97	0.7	2.3	100	99	0.1	0.2
Ca	85200	-	-	-	-	-	-	-	
Cd	2	20	93	0.7	1.0	100	94	0.2	0.4
Co	5.5	20	96	3.5	7.7	100	93	0.8	2.1
Cr	79.7	20	87	28.8	16.5	100	104	1.3	1.1
Cu	113	20	110	16.2	4.4	100	104	4.0	4.2
Fe	16500	-	-	-	-	-	-	-	
Hg	<1.4	10	92	2.5	7.7	40	98	0.0	0.0
K	621	500	121	1.3	0.0	2000	107	0.9	1.8
Li	6.7	10	113	3.5	4.4	40	106	0.6	0.6

NMMA Exhibit 3

Mg	24400	500	*	*	8.4	2000	*	*	10.1
Mn	343	20	*	*	8.5	100	95	11.0	1.6
Mo	5.3	20	88	5.3	13.2	100	91	1.4	4.1
Na	195	500	102	2.2	2.4	2000	100	1.5	3.7
Ni	15.6	20	100	1.8	0.0	100	94	1.5	3.6
P	595	500	106	13.4	8.0	2000	103	3.2	2.7
Pb	145	20	88	51.8	17.9	100	108	15.6	17.4
Sb	6.1	20	83	3.9	7.5	100	81	1.9	5.9
Se	<5	20	79	14.7	52.4	100	99	0.7	2.1
Sn	16.6	20	91	34.6	5.8	80	112	8.7	2.8
Sr	102	100	84	9.6	10.8	400	94	2.5	4.6
Tl	<4	20	92	4.8	14.6	100	91	1.5	4.6
V	16.7	20	104	4.2	5.4	100	99	0.8	1.7
Zn	131	20	103	31.2	7.3	100	104	7.2	6.4
EPA Electroplating Sludge #286									
Ag	6	20	96	0.2	0.	100	93	0.1	0.

NMMA Exhibit 3

					4				4
Al	4980	20	*	*	4.4	100	*	*	5.6
As	32	20	94	1.3	0.8	100	97	0.7	1.6
B	210	100	113	2.0	1.6	400	98	1.9	3.5
Ba	39.8	20	0	6.8	0.3	100	0	1.6	5.7
Be	0.32	20	96	0.2	0.5	100	101	0.7	2.0
Ca	48500	-	-	-	-	-	-	-	
Cd	108	20	98	2.5	0.8	100	96	0.5	0.5
Co	5.9	20	93	2.9	5.7	100	93	0.6	1.5
Cr	7580	20	*	*	0.7	100	*	*	1.3
Cu	806	20	*	*	1.5	100	94	8.3	0.7
Fe	31100	-	-	-	-	-	-	-	
Hg	6.1	10	90	2.5	4.0	40	97	1.7	4.3
K	2390	500	75	8.3	4.0	2000	94	2.9	3.8
Li	9.1	10	101	2.8	0.5	40	106	1.6	3.1
Mg	1950	500	110	2.0	0.8	2000	108	2.3	3.2
Mn	262	20	*	*	1.8	100	91	1.2	0.9
Mo	13.2	20	92	2.1	2.9	100	92	0.3	0.0

NMMA Exhibit 3

Na	73400	500	*	*	1.7	2000	*	*	1.4
Ni	456	20	*	*	0.4	100	88	2.7	0.9
P	9610	500	*	*	2.9	2000	114	7.4	3.4
Pb	1420	20	*	*	2.1	100	*	*	1.3
Sb	<2	20	76	0.9	3.3	100	75	2.8	10.7
Se	6.3	20	86	9.0	16.6	100	103	1.6	2.7
Sn	24.0	20	87	4.0	2.7	80	92	0.7	0.0
Sr	145	100	90	8.1	8.1	400	93	2.4	4.6
Tl	16	20	89	4.6	5.3	100	92	0.8	0.9
V	21.7	20	95	1.2	1.0	100	96	0.4	0.9
Zn	12500	20	*	*	0.8	100	*	*	0.8
NBS 1645 River Sediment									
Ag	1.6	20	92	0.4	1.0	100	96	0.3	0.9
Al	5160	20	*	*	8.4	100	*	*	2.4
As	62.8	20	89	14.4	9.7	100	97	2.9	5.0
B	31.9	100	116	7.1	13.5	400	95	0.6	1.5
Ba	54.8	20	95	6.1	2.8	100	98	1.2	1.3

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Be	0.72	20	101	0.4	1.0	100	103	1.4	3.9
Ca	28000	-	-	-	-	-	-	-	
Cd	9.7	20	100	1.1	0.0	100	101	0.7	1.8
Co	9.4	20	98	3.8	4.8	100	98	0.9	1.8
Cr	28500	20	*	*	0.4	100	*	*	0.7
Cu	109	20	115	8.5	0.0	100	102	1.8	1.0
Fe	84800	-	-	-	-	-	-	-	
Hg	3.1	10	99	4.3	7.7	40	96	0.7	1.0
K	452	500	98	4.1	2.0	2000	106	1.4	2.3
Li	3.7	10	101	2.0	0.7	40	108	1.3	3.0
Mg	6360	500	*	*	1.8	2000	93	2.7	1.0
Mn	728	20	*	*	3.5	100	97	12.4	2.2
Mo	17.9	20	97	12.5	18.5	100	98	0.6	0.0
Na	1020	500	92	2.6	0.0	2000	97	1.1	1.7
Ni	36.2	20	94	5.9	4.0	100	100	1.1	1.5
P	553	500	102	1.4	0.9	2000	100	0.8	1.6
Pb	707	20	*	*	0.8	100	103	5.9	0.4

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Sb	22.8	20	86	2.3	0.0	100	88	0.6	0.9
Se	6.7	20	103	14.3	27.1	100	98	3.1	7.6
Sn	309	20	*	*	1.0	80	101	7.9	2.7
Sr	782	100	91	12.3	3.0	400	96	3.3	2.6
Tl	<4	20	90	0.0	0.0	100	95	1.3	4.0
V	20.1	20	89	5.4	5.8	100	98	0.7	0.0
Zn	1640	20	*	*	1.8	100	*	*	1.1

S (R) Standard deviation of percent recovery.

RPD Relative percent difference between duplicate spike determinations.

< Sample concentration below established method detection limit.

* Spike concentration <10% of sample background concentration.

- Not spiked.

+ Equivalent.

Table 8—ICP-AES Instrumental Precision and Accuracy for Aqueous Solutions[a]

Element	Mean conc. (mg/L)	N[b]	RSD (%)	Accurace[c] (% of Nominal)
Al	14.8	8	6.3	100
Sb	15.1	8	7.7	102
As	14.7	7	6.4	99
Ba	3.66	7	3.1	99
Be	3.78	8	5.8	102

Cd	3.61	8	7.0	97
Ca	15.0	8	7.4	101
Cr	3.75	8	8.2	101
Co	3.52	8	5.9	95
Cu	3.58	8	5.6	97
Fe	14.8	8	5.9	100
Pb	14.4	7	5.9	97
Mg	14.1	8	6.5	96
Mn	3.70	8	4.3	100
Mo	3.70	8	6.9	100
Ni	3.70	7	5.7	100
K	14.1	8	6.6	95
Se	15.3	8	7.5	104
Na	14.0	8	4.2	95
Tl	15.1	7	8.5	102
V	3.51	8	6.6	95
Zn	3.57	8	8.3	96

Table 9—Multilaboratory ICP Precision and Accuracy Data *

Analyte	Concentration	Total recoverable digestion
	μg/L	μg/L
Aluminum	69-4792	X = 0.9380 (C) + 22.1

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.....		SR = 0.0481 (X) + 18.8
Antimony	77-1406	0.8908 (C) + 0.9
.....		SR = 0.0682 (X) + 2.5
Arsenic	69-1887	X = 1.0175 (C) + 3.9
.....		SR = 0.0643 (X) + 10.3
Barium	9-377	X = 0.8.80 (C) + 1.68
.....		SR = 0.0826 (X) + 3.54
Beryllium	3-1906	X = 1.0177 (C) - 0.55
.....		SR = 0.0445 (X) - 0.10
Boron	19-5189	X = 0.9676 (C) + 18.7
.....		SR = 0.0743 (X) + 21.1
Cadmium	9-1943	X = 1.0137 (C) - 0.65
.....		SR = 0.0332 (X) + 0.90
Calcium	17-47170	X = 0.9658 (C) + 0.8
.....		SR = 0.0327 (X) + 10.1
Chromium	13-1406	X = 1.0049 (C) - 1.2
.....		SR = 0.0571 (X) + 1.0
Cobalt	17-2340	X = 0.9278 (C) + 1.5

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.....		SR = 0.0407 (X) + 0.4
Copper.....	8-1887	X = 0.9647 (C) - 3.64
.....		SR = 0.0406 (X) + 0.96
Iron.....	13-9359	X = 0.9830 (C) + 5.7
.....		SR = 0.0790 (X) + 11.5
Lead	42-4717	X = 1.0056 (C) + 4.1
.....		SR = 0.0448 (X) + 3.5
Magnesium.....	34-13868	X = 0.9879 (C) + 2.2
.....		SR = 0.0268 (X) + 8.1
Manganese.....	4-1887	X = 0.9725 (C) + 0.07
.....		SR = 0.0400 (X) + 0.82
Molybdenum.....	17-1830	X = 0.9707 (C) - 2.3
.....		SR = 0.0529 (X) + 2.1
Nickel.....	17-47170	X = 0.9869 (C) + 1.5
.....		SR = 0.0393 (X) + 2.2
Potassium.....	347-14151	X = 0.9355 (C) - 183.1
.....		SR = 0.0329 (X) + 60.9
Selenium.....	69-1415	X = 0.9737 (C) - 1.0

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.....		SR = 0.0443 (X) + 6.6
Silicon	189-9434	X = 0.9737 (C) - 22.6
.....		SR = 0.2133 (X) + 22.6
Silver	8-189	X = 0.3987 (C) + 8.25
.....		SR = 0.1836 (X) - 0.27
Sodium.....	35-47170	X = 1.0526 (C) + 26.7
.....		SR = 0.0884 (X) + 50.5
Thallium	79-1434	X = 0.9238 (C) + 5.5
.....		SR = 0.0106 (X) + 48.0
Vanadium.....	13-4698	X = 0.9551 (C) + 0.4
.....		SR = 0.0472 (X) + 0.5
Zinc	7-7076	X = 0.9500 (C) + 1.82
.....		SR = 0.0153 (X) + 7.78

* —Regression equations abstracted from Reference 16.

X = Mean Recovery, μg/L.

C = True Value for the Concentration, μg/L.

SR = Single-analyst Standard Deviation, μg/L.

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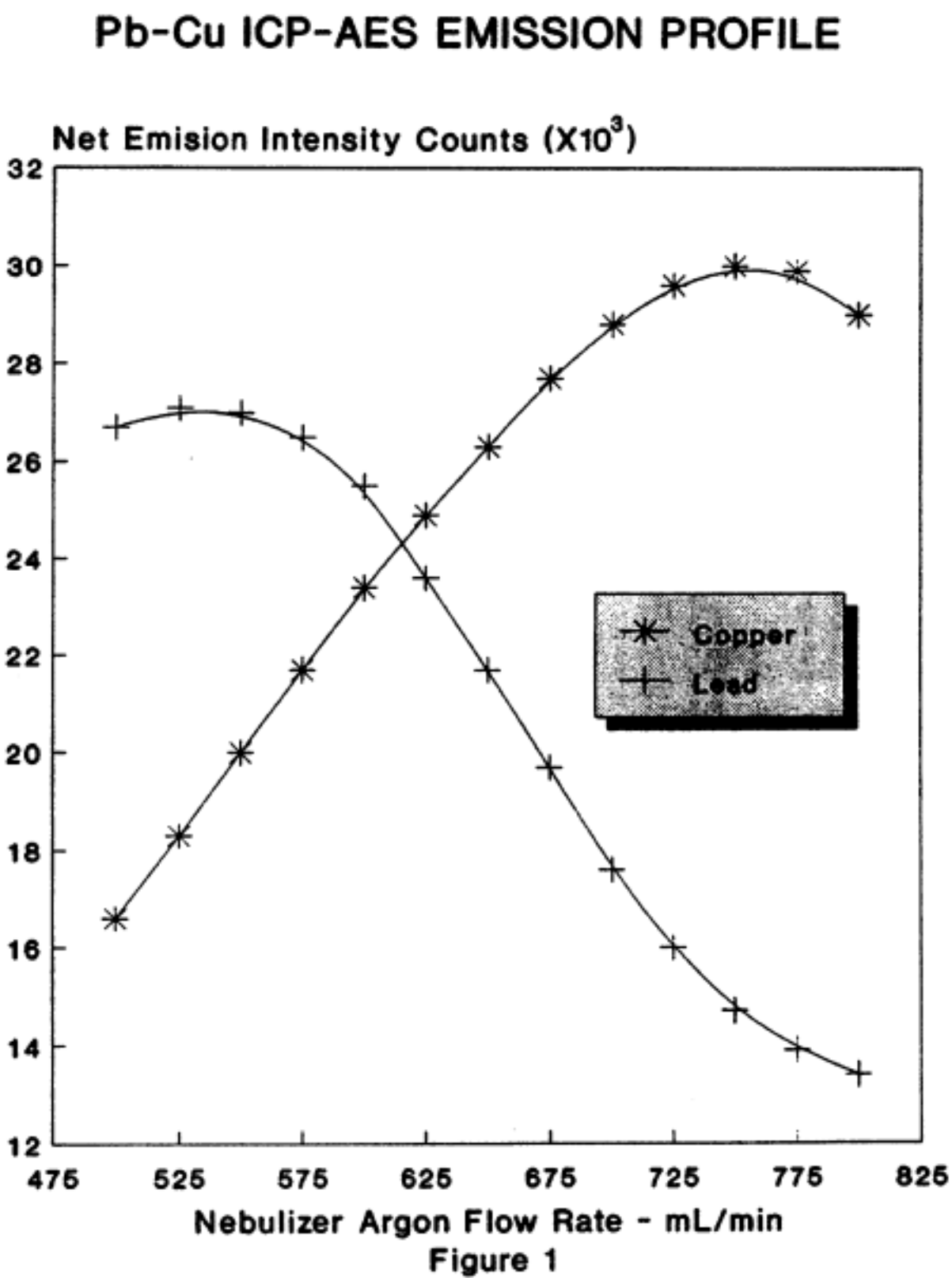

Figure 1

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Credits

[49 FR 43431, Oct. 26, 1984; 50 FR 695, 696, Jan. 4, 1985; 51 FR 23702, June 30, 1986; 55 FR 33440, Aug. 15, 1990; 77 FR 29813, May 18, 2012]

AUTHORITY: Secs. 301, 304(h), 307 and 501(a), Pub.L. 95–217, 91 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).

Current through April 16, 2021; 86 FR 20036

Footnotes

[a] Cerium has been included as method analyte for correction of potential interelement spectral interference.

[b] This method is not suitable for the determination of silica in solids.

[a] The wavelengths listed are recommended because of their sensitivity and overall acceptability. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Section 4.1).

[b] These estimated 3-sigma instrumental detection limits 16 are provided only as a guide to instrumental limits. The method detection limits are sample dependent and may vary as the sample matrix varies. Detection limits for solids can be estimated by dividing these values by the grams extracted per liter, which depends upon the extraction procedure. Divide solution detection limits by 10 for 1 g extracted to 100 mL for solid detection limits.

[c] Suggested concentration for instrument calibration.[2] Other calibration limits in the linear ranges may be used.

[d] Calculated from 2-sigma data.5

[e] Highly dependent on operating conditions and plasma position.

* These on-line interferences from method analytes and titanium only were observed using an instrument with 0.035 nm resolution (see Section 4.1.2). Interferant ranked by magnitude of intensity with the most severe interferant listed first in the row.

[1] MDL concentrations are computed for original matrix with allowance for 2x sample preconcentration during preparation. Samples were processed in PTFE and diluted in 50-mL plastic centrifuge tubes.

[2] Estimated, calculated from aqueous MDL determinations.

* Elevated value due to fume-hood contamination.

* Spike concentration <10% of sample background concentration.

[a] These performance values are independent of sample preparation because the labs analyzed portions of the same solutions using sequential or simultaneous instruments.

[b] N = Number of measurements for mean and relative standard deviation (RSD).

[c] Accuracy is expressed as a percentage of the nominal value for each analyte in the acidified, multi-element solutions.

End of Document

NMMA Exhibit 3

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Method 200.7, Revision 4.4: Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry

METHOD 200.7

DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER AND WASTES BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

Revision 4.4
EMMC Version

USEPA-ICP Users Group (Edited by T.D. Martin and J.F. Kopp) - Method 200.7, Revision 1.0, (Printed 1979, Published 1982)

T.D. Martin and E.R. Martin - Method 200.7, Revision 3.0 (1990)

T.D. Martin, C.A. Brockhoff, J.T. Creed, and S.E. Long (Technology Applications Inc.) - Method 200.7, Revision 3.3 (1991)

T.D. Martin, C.A. Brockhoff, J.T. Creed, and EMMC Methods Work Group - Method 200.7, Revision 4.4 (1994)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

NMMA Exhibit 4

METHOD 200.7

DETERMINATION OF METALS AND TRACE ELEMENTS IN WATER AND WASTES BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is used to determine metals and some nonmetals in solution. This method is a consolidation of existing methods for water, wastewater, and solid wastes.[1-4] (For analysis of petroleum products see References 5 and 6, Section 16.0) This method is applicable to the following analytes:

Analyte		Chemical Abstract Services Registry Number (CASRN)
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Boron	(B)	7440-42-8
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Cerium[a]	(Cr)	7440-45-1
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Lithium	(Li)	7439-93-2
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Phosphorus	(P)	7723-14-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silica[b]	(SiO_2)	7631-86-9
Silver	(Ag)	7440-22-4

[a]Cerium has been included as method analyte for correction of potential interelement spectral interference.

[b]This method is <u>not</u> suitable for the determination of silica in solids.

Analyte		Chemical Abstract Services Registry Number (CASRN)
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Tin	(Sn)	7440-31-5
Titanium	(Ti)	7440-32-6
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

1.2 For reference where this method is approved for use in compliance monitoring programs [e.g., Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)] consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 § 141.23 for drinking water), and the latest Federal Register announcements.

1.3 ICP-AES can be used to determine dissolved analytes in aqueous samples after suitable filtration and acid preservation. To reduce potential interferences, dissolved solids should be <0.2% (w/v) (Section 4.2).

1.4 With the exception of silver, where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, samples may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has turbidity of <1 NTU at the time of analysis. This total recoverable determination procedure is referred to as "direct analysis". However, in the determination of some primary drinking water metal contaminants, preconcentration of the sample may be required prior to analysis in order to meet drinking water acceptance performance criteria (Sections 11.2.2 through 11.2.7).

1.5 For the determination of total recoverable analytes in aqueous and solid samples a digestion/extraction is required prior to analysis when the elements are not in solution (e.g., soils, sludges, sediments and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing suspended or particulate material ≥ 1% (w/v) should be extracted as a solid type sample.

1.6 When determining boron and silica in aqueous samples, only plastic, PTFE or quartz labware should be used from time of sample collection to completion of analysis. For accurate determination of boron in solid samples only quartz or PTFE beakers should be used during acid extraction with immediate transfer of an extract aliquot to a plastic centrifuge tube following dilution of the extract to volume. When possible, borosilicate glass should be avoided to prevent contamination of these analytes.

1.7 Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved analyte or by "direct analysis" where the sample has not been processed using the total recoverable mixed acid digestion. For this reason it is recommended that samples be digested prior to the determination of silver. The total recoverable sample digestion procedure given in this method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well mixed aliquots should be prepared until the analysis solution contains <0.1 mg/L silver. The extraction of solid samples containing concentrations of silver >50 mg/kg should be treated in a similar manner. Also, the extraction of tin from solid samples should be prepared again using aliquots <1 g when determined sample concentrations exceed 1%.

1.8 The total recoverable sample digestion procedure given in this method will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

1.9 The total recoverable sample digestion procedure given in this method is not suitable for the determination of volatile organo-mercury compounds. However, if digestion is not required (turbidity <1 NTU), the combined concentrations of inorganic and organo-mercury in solution can be determined by "direct analysis" pneumatic nebulization provided the sample solution is adjusted to contain the same mixed acid (HNO_3 + HCl) matrix as the total recoverable calibration standards and blank solutions.

1.10 Detection limits and linear ranges for the elements will vary with the wavelength selected, the spectrometer, and the matrices. Table 1 provides estimated instrument detection limits for the listed wavelengths.[7] However, actual method detection limits and linear working ranges will be dependent on the sample matrix, instrumentation, and selected operating conditions.

1.11 Users of the method data should state the data-quality objectives prior to analysis. Users of the method must document and have on file the required initial demonstration performance data described in Section 9.2 prior to using the method for analysis.

2.0 SUMMARY OF METHOD

2.1 An aliquot of a well mixed, homogeneous aqueous or solid sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous sample containing undissolved material, analytes are first solubilized by gentle refluxing with nitric and hydrochloric

acids. After cooling, the sample is made up to volume, is mixed and centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved analytes in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of analytes in drinking water where sample turbidity is <1 NTU, the sample is made ready for analysis by the appropriate addition of nitric acid, and then diluted to a predetermined volume and mixed before analysis.

2.2 The analysis described in this method involves multielemental determinations by ICP-AES using sequential or simultaneous instruments. The instruments measure characteristic atomic-line emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the line spectra are monitored at specific wavelengths by a photosensitive device. Photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of the analytes. Background must be measured adjacent to the analyte wavelength during analysis. Various interferences must be considered and addressed appropriately as discussed in Sections 4.0, 7.0, 9.0, 10.0, and 11.0.

3.0 DEFINITIONS

3.1 **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 7.10.1).

3.2 **Calibration Standard (CAL)** - A solution prepared from the dilution of stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration (Section 7.9).

3.3 **Dissolved Analyte** - The concentration of analyte in an aqueous sample that will pass through a 0.45 µm membrane filter assembly prior to sample acidification (Section 11.1).

3.4 **Field Reagent Blank (FRB)** - An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment (Section 8.5).

3.5 **Instrument Detection Limit (IDL)** - The concentration equivalent to the analyte signal which is equal to three times the standard deviation of a series of 10 replicate measurements of the calibration blank signal at the same wavelength (Table 1.).

3.6 **Instrument Performance Check (IPC) Solution** - A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria (Sections 7.11 and 9.3.4).

3.7 **Internal Standard** - Pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component (Section 11.5).

3.8 **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.

3.9 **Laboratory Fortified Blank (LFB)** - An aliquot of LRB to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control and whether the laboratory is capable of making accurate and precise measurements (Sections 7.10.3 and 9.3.2).

3.10 **Laboratory Fortified Sample Matrix (LFM)** - An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations (Section 9.4).

3.11 **Laboratory Reagent Blank (LRB)** - An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus (Sections 7.10.2 and 9.3.1).

3.12 **Linear Dynamic Range (LDR)** - The concentration range over which the instrument response to an analyte is linear (Section 9.2.2).

3.13 **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 9.2.4 and Table 4.).

3.14 **Plasma Solution** - A solution that is used to determine the optimum height above the work coil for viewing the plasma (Sections 7.15 and 10.2.3).

3.15 **Quality Control Sample (QCS)** - A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check either laboratory or instrument performance (Sections 7.12 and 9.2.3).

3.16 **Solid Sample** - For the purpose of this method, a sample taken from material classified as either soil, sediment or sludge.

3.17 **Spectral Interference Check (SIC) Solution** - A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting known interelement spectral interferences with respect to a defined set of method criteria (Sections 7.13, 7.14 and 9.3.5).

3.18 **Standard Addition** - The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response is then used to assess either an operative matrix effect or the sample analyte concentration (Sections 9.5.1 and 11.5).

3.19 **Stock Standard Solution** - A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source (Section 7.8).

3.20 **Total Recoverable Analyte** - The concentration of analyte determined either by "direct analysis" of an unfiltered acid preserved drinking water sample with turbidity of <1 NTU (Section 11.2.1), or by analysis of the solution extract of a solid sample or an unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method (Sections 11.2 and 11.3).

3.21 **Water Sample** - For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm runoff, industrial or domestic wastewater.

4.0 INTERFERENCES

4.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

4.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurement(s) adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate not only when alternate wavelengths are desirable because of severe spectral interference, but also will show whether the most appropriate estimate

of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by the measured emission on one side or the other. The location(s) selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The location(s) used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak.

4.1.2 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated for by equations that correct for interelement contributions, which involves measuring the interfering elements. Some potential on-line spectral interferences observed for the recommended wavelengths are given in Table 2. When operative and uncorrected, these interferences will produce false-positive determinations and be reported as analyte concentrations. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature that were observed with a single instrument having a working resolution of 0.035 nm are listed. More extensive information on interferant effects at various wavelengths and resolutions is available in Boumans' Tables.[8] Users may apply interelement correction factors determined on their instruments within tested concentration ranges to compensate (off-line or on-line) for the effects of interfering elements.

4.1.3 When interelement corrections are applied, there is a need to verify their accuracy by analyzing spectral interference check solutions as described in Section 7.13. Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating plus the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences.[7,8]

4.1.4 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths given in Table 1, the analyst is required to determine and document for each wavelength the effect from the known interferences given in Table 2, and to utilize a computer routine for their automatic

correction on all analyses. To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must be either free of off-line interelement spectral interference or a computer routine must be used for their automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the user must determine and document both the on-line and off-line spectral interference effect from all method analytes and provide for their automatic correction on all analyses. Tests to determine the spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient, however, for analytes such as iron that may be found at high concentration a more appropriate test would be to use a concentration near the upper LDR limit. See Section 10.4 for required spectral interference test criteria.

4.1.5 When interelement corrections are *not* used, either on-going SIC solutions (Section 7.14) must be analyzed to verify the absence of interelement spectral interference or a computer software routine must be employed for comparing the determinative data to limits files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration, greater than the analyte IDL, or false negative analyte concentration, less than the 99% lower control limit of the calibration blank. When the interference accounts for 10% or more of the analyte concentration, either an alternate wavelength free of interference or another approved test procedure must be used to complete the analysis. For example, the copper peak at 213.853 nm could be mistaken for the zinc peak at 213.856 nm in solutions with high copper and low zinc concentrations. For this example, a spectral scan in the 213.8 nm region would not reveal the misidentification because a single peak near the zinc location would be observed. The possibility of this misidentification of copper for the zinc peak at 213.856 nm can be identified by measuring the copper at another emission line, e.g., 324.754 nm. Users should be aware that, depending upon the instrumental resolution, alternate wavelengths with adequate sensitivity and freedom from interference may not be available for all matrices. In these circumstances the analyte must be determined using another approved test procedure.

4.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by such means as a high-solids nebulizer, diluting the sample,

using a peristaltic pump, or using an appropriate internal standard element. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. This problem can be controlled by a high-solids nebulizer, wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Also, it has been reported that better control of the argon flow rates, especially for the nebulizer, improves instrument stability and precision; this is accomplished with the use of mass flow controllers.

4.3 Chemical interferences include molecular-compound formation, ionization effects, and solute-vaporization effects. Normally, these effects are not significant with the ICP-AES technique. If observed, they can be minimized by careful selection of operating conditions (such as incident power and observation height), by buffering of the sample, by matrix matching, and by standard-addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.4 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples (Section 7.10.4). The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements corresponding to either their LDR or a concentration ten times those usually encountered. The aspiration time should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit, should be noted. Until the required rinse time is established, this method requires a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be re-analyzed after a long rinse period.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method.[9-12] A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Specifically, 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 safety glasses or a shield for eye protection, protective clothing and observe proper mixing when working with these reagents.

5.2 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification of samples should be done in a fume hood.

5.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease causative agents.

5.4 The inductively coupled plasma should only be viewed with proper eye protection from the ultraviolet emissions.

5.5 It is the responsibility of the user of this method to comply with relevant disposal and waste regulations. For guidance see Sections 14.0 and 15.0.

6.0 EQUIPMENT AND SUPPLIES

6.1 Inductively coupled plasma emission spectrometer:

6.1.1 Computer-controlled emission spectrometer with background-correction capability. The spectrometer must be capable of meeting and complying with the requirements described and referenced in Section 2.2.

6.1.2 Radio-frequency generator compliant with FCC regulations.

6.1.3 Argon gas supply - High purity grade (99.99%). When analyses are conducted frequently, liquid argon is more economical and requires less frequent replacement of tanks than compressed argon in conventional cylinders.

6.1.4 A variable speed peristaltic pump is required to deliver both standard and sample solutions to the nebulizer.

6.1.5 (Optional) Mass flow controllers to regulate the argon flow rates, especially the aerosol transport gas, are highly recommended. Their use will provide more exacting control of reproducible plasma conditions.

6.2 Analytical balance, with capability to measure to 0.1 mg, for use in weighing solids, for preparing standards, and for determining dissolved solids in digests or extracts.

6.3 A temperature adjustable hot plate capable of maintaining a temperature of 95°C.

6.4 (Optional) A temperature adjustable block digester capable of maintaining a temperature of 95°C and equipped with 250 mL constricted digestion tubes.

6.5 (Optional) A steel cabinet centrifuge with guard bowl, electric timer and brake.

6.6 A gravity convection drying oven with thermostatic control capable of maintaining 180°C ± 5°C.

6.7 (Optional) An air displacement pipetter capable of delivering volumes ranging from 0.1-2500 µL with an assortment of high quality disposable pipet tips.

6.8 Mortar and pestle, ceramic or nonmetallic material.

6.9 Polypropylene sieve, 5-mesh (4 mm opening).

6.10 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 designated for trace element sample handling must be used. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching, (2) depleting element concentrations through adsorption processes. All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. Several procedures found to provide clean labware include washing with a detergent solution, rinsing with tap water, soaking for four hours or more in 20% (v/v) nitric acid or a mixture of HNO_3 and HCl (1+2+9), rinsing with reagent water and storing clean.[2,3] Chromic acid cleaning solutions must be avoided because chromium is an analyte.

6.10.1 Glassware - Volumetric flasks, graduated cylinders, funnels and centrifuge tubes (glass and/or metal-free plastic).

6.10.2 Assorted calibrated pipettes.

6.10.3 Conical Phillips beakers (Corning 1080-250 or equivalent), 250 mL with 50 mm watch glasses.

6.10.4 Griffin beakers, 250 mL with 75 mm watch glasses and (optional) 75 mm ribbed watch glasses.

6.10.5 (Optional) PTFE and/or quartz Griffin beakers, 250 mL with PTFE covers.

6.10.6 Evaporating dishes or high-form crucibles, porcelain, 100 mL capacity.

6.10.7 Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125 mL to 1 L capacities.

6.10.8 One-piece stem FEP wash bottle with screw closure, 125 mL capacity.

7.0 REAGENTS AND STANDARDS

7.1 Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society specifications[13] should be used whenever possible. If the purity of a reagent is in question, analyze for contamination. All acids used for this method must be of ultra high-purity grade or equivalent. Suitable acids are available from a number of manufacturers. Redistilled acids prepared by sub-boiling distillation are acceptable.

7.2 Hydrochloric acid, concentrated (sp.gr. 1.19) - HCl.

7.2.1 Hydrochloric acid (1+1) - Add 500 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

7.2.2 Hydrochloric acid (1+4) - Add 200 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

7.2.3 Hydrochloric acid (1+20) - Add 10 mL concentrated HCl to 200 mL reagent water.

7.3 Nitric acid, concentrated (sp.gr. 1.41) - HNO_3.

7.3.1 Nitric acid (1+1) - Add 500 mL concentrated HNO_3 to 400 mL reagent water and dilute to 1 L.

7.3.2 Nitric acid (1+2) - Add 100 mL concentrated HNO_3 to 200 mL reagent water.

7.3.3 Nitric acid (1+5) - Add 50 mL concentrated HNO_3 to 250 mL reagent water.

7.3.4 Nitric acid (1+9) - Add 10 mL concentrated HNO_3 to 90 mL reagent water.

7.4 Reagent water. All references to water in this method refer to ASTM Type I grade water.[14]

7.5 Ammonium hydroxide, concentrated (sp. gr. 0.902).

7.6 Tartaric acid, ACS reagent grade.

7.7 Hydrogen peroxide, 50%, stabilized certified reagent grade.

7.8 Standard Stock Solutions - Stock standards may be purchased or prepared from ultra-high purity grade chemicals (99.99-99.999% pure). All compounds must be dried for one hour at 105°C, unless otherwise specified. It is recommended that stock solutions be stored in FEP bottles. Replace stock standards when succeeding dilutions for preparation of calibration standards cannot be verified.

CAUTION: Many of these chemicals are extremely toxic if inhaled or swallowed (Section 5.1). Wash hands thoroughly after handling.

Typical stock solution preparation procedures follow for 1 L quantities, but for the purpose of pollution prevention, the analyst is encouraged to prepare smaller quantities when possible. Concentrations are calculated based upon the weight of the pure element or upon the weight of the compound multiplied by the fraction of the analyte in the compound.

From pure element,

$$\text{Concentration} = \frac{\text{weight (mg)}}{\text{volume (L)}}$$

From pure compound,

$$\text{Concentration} = \frac{\text{weight (mg) x gravimetric factor}}{\text{volume (L)}}$$

where: gravimetric factor = the weight fraction of the analyte in the compound

7.8.1 Aluminum solution, stock, 1 mL = 1000 µg Al: Dissolve 1.000 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4.0 mL of (1+1) HCl and 1 mL of concentrated $HN0_3$ in a beaker. Warm beaker slowly to effect solution. When dissolution is complete, transfer solution quantitatively to a 1 L flask, add an additional 10.0 mL of (1+1) HCl and dilute to volume with reagent water.

7.8.2 Antimony solution, stock, 1 mL = 1000 µg Sb: Dissolve 1.000 g of antimony powder, weighed accurately to at least four significant figures, in 20.0 mL (1+1) HNO_3 and 10.0 mL concentrated HCl. Add 100 mL reagent water and 1.50 g tartaric acid. Warm solution slightly

to effect complete dissolution. Cool solution and add reagent water to volume in a 1 L volumetric flask.

7.8.3 Arsenic solution, stock, 1 mL = 1000 µg As: Dissolve 1.320 g of As_2O_3 (As fraction = 0.7574), weighed accurately to at least four significant figures, in 100 mL of reagent water containing 10.0 mL concentrated NH_4OH. Warm the solution gently to effect dissolution. Acidify the solution with 20.0 mL concentrated HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.4 Barium solution, stock, 1 mL = 1000 µg Ba: Dissolve 1.437 g $BaCO_3$ (Ba fraction = 0.6960), weighed accurately to at least four significant figures, in 150 mL (1+2) HNO_3 with heating and stirring to degas and dissolve compound. Let solution cool and dilute with reagent water in 1 L volumetric flask.

7.8.5 Beryllium solution, stock, 1 mL = 1000 µg Be: DO NOT DRY. Dissolve 19.66 g $BeSO_4 \cdot 4H_2O$ (Be fraction = 0.0509), weighed accurately to at least four significant figures, in reagent water, add 10.0 mL concentrated HNO_3, and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.6 Boron solution, stock, 1 mL = 1000 µg B: DO NOT DRY. Dissolve 5.716 g anhydrous H_3BO_3 (B fraction = 0.1749), weighed accurately to at least four significant figures, in reagent water and dilute in a 1 L volumetric flask with reagent water. Transfer immediately after mixing to a clean FEP bottle to minimize any leaching of boron from the glass volumetric container. Use of a nonglass volumetric flask is recommended to avoid boron contamination from glassware.

7.8.7 Cadmium solution, stock, 1 mL = 1000 µg Cd: Dissolve 1.000 g Cd metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1 L volumetric flask.

7.8.8 Calcium solution, stock, 1 mL = 1000 µg Ca: Suspend 2.498 g $CaCO_3$ (Ca fraction = 0.4005), dried at 180°C for one hour before weighing, weighed accurately to at least four significant figures, in reagent water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.9 Cerium solution, stock, 1 mL = 1000 µg Ce: Slurry 1.228 g CeO_2 (Ce fraction = 0.8141), weighed accurately to at least four significant figures, in 100 mL concentrated HNO_3 and evaporate to dryness. Slurry the residue in 20 mL H_2O, add 50 mL concentrated HNO_3, with heat and stirring add 60 mL 50% H_2O_2 dropwise in 1 mL increments

allowing periods of stirring between the 1 mL additions. Boil off excess H_2O_2 before diluting to volume in a 1 L volumetric flask with reagent water.

7.8.10 Chromium solution, stock, 1 mL = 1000 µg Cr: Dissolve 1.923 g CrO_3 (Cr fraction = 0.5200), weighed accurately to at least four significant figures, in 120 mL (1+5) HNO_3. When solution is complete, dilute to volume in a 1 L volumetric flask with reagent water.

7.8.11 Cobalt solution, stock, 1 mL = 1000 µg Co: Dissolve 1.000 g Co metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50.0 mL (1+1) HNO_3. Let solution cool and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.12 Copper solution, stock, 1 mL = 1000 µg Cu: Dissolve 1.000 g Cu metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50.0 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute in a 1 L volumetric flask with reagent water.

7.8.13 Iron solution, stock, 1 mL = 1000 µg Fe: Dissolve 1.000 g Fe metal, acid cleaned with (1+1) HCl, weighed accurately to four significant figures, in 100 mL (1+1) HCl with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1 L volumetric flask.

7.8.14 Lead solution, stock, 1 mL = 1000 µg Pb: Dissolve 1.599 g $Pb(NO_3)_2$ (Pb fraction = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1+1) HNO_3. Add 20.0 mL (1+1) HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.15 Lithium solution, stock, 1 mL = 1000 µg Li: Dissolve 5.324 g Li_2CO_3 (Li fraction = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1+1) HCl and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.16 Magnesium solution, stock, 1 mL = 1000 µg Mg: Dissolve 1.000 g cleanly polished Mg ribbon, accurately weighed to at least four significant figures, in **slowly** added 5.0 mL (1+1) HCl (**CAUTION:** reaction is vigorous). Add 20.0 mL (1+1) HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.17 Manganese solution, stock, 1 mL = 1000 µg Mn: Dissolve 1.000 g of manganese metal, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.18 Mercury solution, stock, 1 mL = 1000 µg Hg: DO NOT DRY. **CAUTION:** highly toxic element. Dissolve 1.354 g $HgCl_2$ (Hg fraction = 0.7388) in reagent water. Add 50.0 mL concentrated HNO_3 and dilute to volume in 1 L volumetric flask with reagent water.

7.8.19 Molybdenum solution, stock, 1 mL = 1000 µg Mo: Dissolve 1.500 g MoO_3 (Mo fraction = 0.6666), weighed accurately to at least four significant figures, in a mixture of 100 mL reagent water and 10.0 mL concentrated NH_4OH, heating to effect dissolution. Let solution cool and dilute with reagent water in a 1 L volumetric flask.

7.8.20 Nickel solution, stock, 1 mL = 1000 µg Ni: Dissolve 1.000 g of nickel metal, weighed accurately to at least four significant figures, in 20.0 mL hot concentrated HNO_3, cool, and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.21 Phosphorus solution, stock, 1 mL = 1000 µg P: Dissolve 3.745 g $NH_4H_2PO_4$ (P fraction = 0.2696), weighed accurately to at least four significant figures, in 200 mL reagent water and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.22 Potassium solution, stock, 1 mL = 1000 µg K: Dissolve 1.907 g KCl (K fraction = 0.5244) dried at 110°C, weighed accurately to at least four significant figures, in reagent water, add 20 mL (1+1) HCl and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.23 Selenium solution, stock, 1 mL = 1000 µg Se: Dissolve 1.405 g SeO_2 (Se fraction = 0.7116), weighed accurately to at least four significant figures, in 200 mL reagent water and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.24 Silica solution, stock, 1 mL = 1000 µg SiO_2: DO NOT DRY. Dissolve 2.964 g $(NH_4)_2SiF_6$, weighed accurately to at least four significant figures, in 200 mL (1+20) HCl with heating at 85°C to effect dissolution. Let solution cool and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.25 Silver solution, stock, 1 mL = 1000 µg Ag: Dissolve 1.000 g Ag metal, weighed accurately to at least four significant figures, in 80 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1 L volumetric flask. Store solution in amber bottle or wrap bottle completely with aluminum foil to protect solution from light.

7.8.26 Sodium solution, stock, 1 mL = 1000 µg Na: Dissolve 2.542 g NaCl (Na fraction = 0.3934), weighed accurately to at least four significant figures, in reagent water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.27 Strontium solution, stock, 1 mL = 1000 µg Sr: Dissolve 1.685 g $SrCO_3$ (Sr fraction = 0.5935), weighed accurately to at least four significant figures, in 200 mL reagent water with dropwise addition of 100 mL (1+1) HCl. Dilute to volume in a 1 L volumetric flask with reagent water.

7.8.28 Thallium solution, stock, 1 mL = 1000 µg Tl: Dissolve 1.303 g $TlNO_3$ (Tl fraction = 0.7672), weighed accurately to at least four significant figures, in reagent water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.29 Tin solution, stock, 1 mL = 1000 µg Sn: Dissolve 1.000 g Sn shot, weighed accurately to at least four significant figures, in an acid mixture of 10.0 mL concentrated HCl and 2.0 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool, add 200 mL concentrated HCl, and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.30 Titanium solution, stock, 1 mL = 1000 µg Ti: DO NOT DRY. Dissolve 6.138 g $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$ (Ti fraction = 0.1629), weighed accurately to at least four significant figures, in 100 mL reagent water. Dilute to volume in a 1 L volumetric flask with reagent water.

7.8.31 Vanadium solution, stock, 1 mL = 1000 µg V: Dissolve 1.000 g V metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water to volume in a 1 L volumetric flask.

7.8.32 Yttrium solution, stock 1 mL = 1000 µg Y: Dissolve 1.270 g Y_2O_3 (Y fraction = 0.7875), weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3, heating to effect dissolution. Cool and dilute to volume in a 1 L volumetric flask with reagent water.

7.8.33 Zinc solution, stock, 1 mL = 1000 µg Zn: Dissolve 1.000 g Zn metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water to volume in a 1 L volumetric flask.

7.9 Mixed Calibration Standard Solutions - For the analysis of total recoverable digested samples prepare mixed calibration standard solutions (see Table 3) by combining appropriate volumes of the stock solutions in 500 mL volumetric flasks containing 20 mL (1+1) HNO_3 and 20 mL (1+1) HCl and dilute to volume with reagent water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and

stable together. To minimize the opportunity for contamination by the containers, it is recommended to transfer the mixed-standard solutions to acid-cleaned, never-used FEP fluorocarbon (FEP) bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentrations can change on aging. Calibration standards not prepared from primary standards must be initially verified using a certified reference solution. For the recommended wavelengths listed in Table 1 some typical calibration standard combinations are given in Table 3.

Note: If the addition of silver to the recommended mixed-acid calibration standard results in an initial precipitation, add 15 mL of reagent water and warm the flask until the solution clears. For this acid combination, the silver concentration should be limited to 0.5 mg/L.

7.10 Blanks - Four types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, the laboratory reagent blank is used to assess possible contamination from the sample preparation procedure, the laboratory fortified blank is used to assess routine laboratory performance and a rinse blank is used to flush the instrument uptake system and nebulizer between standards, check solutions, and samples to reduce memory interferences.

7.10.1 The calibration blank for aqueous samples and extracts is prepared by acidifying reagent water to the same concentrations of the acids as used for the standards. The calibration blank should be stored in a FEP bottle.

7.10.2 The laboratory reagent blank (LRB) must contain all the reagents in the same volumes as used in the processing of the samples. The LRB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

7.10.3 The laboratory fortified blank (LFB) is prepared by fortifying an aliquot of the laboratory reagent blank with all analytes to a suitable concentration using the following recommended criteria: Ag $\leq$ 0.1 mg/L, $\geq$ K 5.0 mg/L and all other analytes 0.2 mg/L or a concentration approximately 100 times their respective MDL, whichever is greater. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable.

7.10.4 The rinse blank is prepared by acidifying reagent water to the same concentrations of acids as used in the calibration blank and stored in a convenient manner.

7.11 Instrument Performance Check (IPC) Solution - The IPC solution is used to periodically verify instrument performance during analysis. It should be prepared in the same acid mixture as the calibration standards by combining method analytes at appropriate concentrations. Silver must be limited to

<0.5 mg/L; while potassium and phosphorus because of higher MDLs and silica because of potential contamination should be at concentrations of 10 mg/L. For other analytes a concentration of 2 mg/L is recommended. The IPC solution should be prepared from the same standard stock solutions used to prepare the calibration standards and stored in an FEP bottle. Agency programs may specify or request that additional instrument performance check solutions be prepared at specified concentrations in order to meet particular program needs.

7.12 Quality Control Sample (QCS) - Analysis of a QCS is required for initial and periodic verification of calibration standards or stock standard solutions in order to verify instrument performance. The QCS must be obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards. The concentration of the analytes in the QCS solution should be ≥ 1 mg/L, except silver, which must be limited to a concentration of 0.5 mg/L for solution stability. The QCS solution should be stored in a FEP bottle and analyzed as needed to meet data-quality needs. A fresh solution should be prepared quarterly or more frequently as needed.

7.13 Spectral Interference Check (SIC) Solutions - When interelement corrections are applied, SIC solutions are needed containing concentrations of the interfering elements at levels that will provide an adequate test of the correction factors.

7.13.1 SIC solutions containing (a) 300 mg/L Fe; (b) 200 mg/L AL; (c) 50 mg/L Ba; (d) 50 mg/L Be; (e) 50 mg/L Cd; (f) 50 mg/L Ce; (g) 50 mg/L Co; (h) 50 mg/L Cr; (i) 50 mg/L Cu; (j) 50 mg/L Mn; (k) 50 mg/L Mo; (l) 50 mg/L Ni; (m) 50 mg/L Sn; (n) 50 mg/L SiO_2; (o) 50 mg/L Ti; (p) 50 mg/L Tl and (q) 50 mg/L V should be prepared in the same acid mixture as the calibration standards and stored in FEP bottles. These solutions can be used to periodically verify a partial list of the on-line (and possible off-line) interelement spectral correction factors for the recommended wavelengths given in Table 1. Other solutions could achieve the same objective as well. (Multielement SIC solutions[3] may be prepared and substituted for the single element solutions provided an analyte is not subject to interference from more than one interferant in the solution.)

Note: If wavelengths other than those recommended in Table 1 are used, other solutions different from those above (a through q) may be required.

7.13.2 For interferences from iron and aluminum, only those correction factors (positive or negative) when multiplied by 100 to calculate apparent analyte concentrations that exceed the determined analyte IDL or fall below the lower 3-sigma control limit of the calibration blank need be tested on a daily basis.

7.13.3 For the other interfering elements, only those correction factors (positive or negative) when multiplied by 10 to calculate apparent analyte concentrations that exceed the determined analyte IDL or fall below the lower 3-sigma control limit of the calibration blank need be tested on a daily basis.

7.13.4 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution (a through q) should fall within a specific concentration range bracketing the calibration blank. This concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and dividing by 10. If after subtraction of the calibration blank the apparent analyte concentration is outside (above or below) this range, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor should be updated.

Note: The SIC solution should be analyzed more than once to confirm a change has occurred with adequate rinse time between solutions and before subsequent analysis of the calibration blank.

7.13.5 If the correction factors tested on a daily basis are found to be within the 10% criteria for five consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such (e.g., finished drinking water) that they do not contain concentrations of the interfering elements at the 10 mg/L level, daily verification is not required; however, all interelement spectral correction factors must be verified annually and updated, if necessary.

7.13.6 If the instrument does not display negative concentration values, fortify the SIC solutions with the elements of interest at 1 mg/L and test for analyte recoveries that are below 95%. In the absence of measurable analyte, over-correction could go undetected because a negative value could be reported as zero.

7.14 For instruments without interelement correction capability or when interelement corrections are not used, SIC solutions (containing similar concentrations of the major components in the samples, e.g., ≥ 10 mg/L) can serve to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the SIC solution confirms an operative interference that is ≥ 10% of the analyte concentration, the analyte must be determined using a wavelength and background correction location free of the interference or by another approved test procedure. Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests.

7.15 Plasma Solution - The plasma solution is used for determining the optimum viewing height of the plasma above the work coil prior to using the method (Section 10.2). The solution is prepared by adding a 5 mL aliquot from each of the stock standard solutions of arsenic, lead, selenium, and thallium to a mixture of 20 mL (1+1) nitric acid and 20 mL (1+1) hydrochloric acid and diluting to 500 mL with reagent water. Store in a FEP bottle.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples **must** be tested immediately prior to aliquoting for processing or "direct analysis" to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to six months before analysis.

8.2 For the determination of the dissolved elements, the sample must be filtered through a 0.45 µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus are recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silica are critical.) Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) nitric acid immediately following filtration to pH <2.

8.3 For the determination of total recoverable elements in aqueous samples, samples are **not** filtered, but acidified with (1+1) nitric acid to pH <2 (normally, 3 mL of (1+1) acid per liter of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection, however, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination it is recommended that the samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for 16 hours, and then verified to be pH <2 just prior withdrawing an aliquot for processing or "direct analysis". If for some reason such as high alkalinity the sample pH is verified to be >2, more acid must be added and the sample held for 16 hours until verified to be pH <2. See Section 8.1.

Note: When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood. See Section 5.2.

8.4 Solid samples require no preservation prior to analysis other than storage at 4°C. There is no established holding time limitation for solid samples.

8.5 For aqueous samples, a field blank should be prepared and analyzed as required by the data user. Use the same container and acid as used in sample collection.

9.0 QUALITY CONTROL

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the periodic analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data thus generated.

9.2 Initial Demonstration of Performance (mandatory).

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of linear dynamic ranges and analysis of quality control samples) and laboratory performance (determination of method detection limits) prior to analyses conducted by this method.

9.2.2 Linear dynamic range (LDR) - The upper limit of the LDR must be established for each wavelength utilized. It must be determined from a linear calibration prepared in the normal manner using the established analytical operating procedure for the instrument. The LDR should be determined by analyzing succeedingly higher standard concentrations of the analyte until the observed analyte concentration is no more than 10% below the stated concentration of the standard. Determined LDRs must be documented and kept on file. The LDR which may be used for the analysis of samples should be judged by the analyst from the resulting data. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and reanalyzed. The LDRs should be verified annually or whenever, in the judgement of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

9.2.3 Quality control sample (QCS) - When beginning the use of this method, on a quarterly basis, after the preparation of stock or calibration standard solutions 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 7.12). To verify the calibration standards the determined mean concentrations from three analyses of the QCS must be within ±5% of the stated values. If the calibration standard cannot be verified, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding on with the initial determination of method detection limits or continuing with on-going analyses.

9.2.4 Method detection limit (MDL) - MDLs must be established for all wavelengths utilized, using reagent water (blank) fortified at a concentration of two to three times the estimated instrument detection limit.[15] To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

Where:

t = students' t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates]

S = standard deviation of the replicate analyses

Note: If additional confirmation is desired, reanalyze the seven replicate aliquots on two more nonconsecutive days and again calculate the MDL values for each day. An average of the three MDL values for each analyte may provide for a more appropriate MDL estimate. If the relative standard deviation (RSD) from the analyses of the seven aliquots is <10%, the concentration used to determine the analyte MDL may have been inapprop-riately high for the determination. If so, this could result in the calculation of an unrealistically low MDL. Concurrently, determination of MDL in reagent water represents a best case situation and does not reflect possible matrix effects of real world samples. However, successful analyses of LFMs (Section 9.4) and the analyte addition test described in Section 9.5.1 can give confidence to the MDL value determined in reagent water. Typical single laboratory MDL values using this method are given in Table 4.

The MDLs must be sufficient to detect analytes at the required levels according to compliance monitoring regulation (Section 1.2). MDLs should be determined annually, when a new operator begins work or whenever, in the judgement of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they be redetermined.

9.3 Assessing Laboratory Performance (mandatory)

9.3.1 Laboratory reagent blank (LRB) - The laboratory must analyze at least one LRB (Section 7.10.2) with each batch of 20 or fewer samples of the same matrix. LRB data are used to assess contamination from the laboratory environment. LRB values that exceed the MDL indicate laboratory or reagent contamination should be suspected. When LRB values constitute 10% or more of the analyte level determined for a

sample or is 2.2 times the analyte MDL whichever is greater, fresh aliquots of the samples must be prepared and analyzed again for the affected analytes after the source of contamination has been corrected and acceptable LRB values have been obtained.

9.3.2 Laboratory fortified blank (LFB) - The laboratory must analyze at least one LFB (Section 7.10.3) with each batch of samples. Calculate accuracy as percent recovery using the following equation:

$$R = \frac{LFB - LRB}{s} X\ 100$$

Where:

R	=	percent recovery
LFB	=	laboratory fortified blank
LRB	=	laboratory reagent blank
s	=	concentration equivalent of analyte added to fortify the LBR solution

If the recovery of any analyte falls outside the required control limits of 85-115%, that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3 The laboratory must use LFB analyses data to assess laboratory performance against the required control limits of 85-115% (Section 9.3.2). When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the mean percent recovery (x) and the standard deviation (S) of the mean percent recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = x + 3S
LOWER CONTROL LIMIT = x - 3S

The optional control limits must be equal to or better than the required control limits of 85-115%. After each five to 10 new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations included in the LFB. These data must be kept on file and be available for review.

9.3.4 Instrument performance check (IPC) solution - For all determinations the laboratory must analyze the IPC solution (Section 7.11) and a calibration blank immediately following daily calibration, after every 10th sample (or more frequently, if required) and at the end of the sample run. Analysis of the calibration blank should always be < the analyte IDL, but greater than the lower 3-sigma control limit of the calibration blank. Analysis of the IPC solution immediately following calibration must verify that the instrument is within ±5% of calibration with a relative standard deviation <3% from replicate integrations ≥ 4. Subsequent analyses of the IPC solution must be within ±10% of calibration. If the calibration cannot be verified within the specified limits, reanalyze either or both the IPC solution and the calibration blank. If the second analysis of the IPC solution or the calibration blank confirm calibration to be outside the limits, sample analysis must be discontinued, the cause determined, corrected and/or the instrument recalibrated. All samples following the last acceptable IPC solution must be reanalyzed. The analysis data of the calibration blank and IPC solution must be kept on file with the sample analyses data.

9.3.5 Spectral interference check (SIC) solution - For all determinations the laboratory must periodically verify the interelement spectral interference correction routine by analyzing SIC solutions. The preparation and required periodic analysis of SIC solutions and test criteria for verifying the interelement interference correction routine are given in Section 7.13. Special cases where on-going verification is required are described in Section 7.14.

9.4 Assessing Analyte Recovery and Data Quality

9.4.1 Sample homogeneity and the chemical nature of the sample matrix can affect analyte recovery and the quality of the data. Taking separate aliquots from the sample for replicate and fortified analyses can in some cases assess the effect. Unless otherwise specified by the data user, laboratory or program, the following laboratory fortified matrix (LFM) procedure (Section 9.4.2) is required. Also, other tests such as the analyte addition test (Section 9.5.1) and sample dilution test (Section 9.5.2) can indicate if matrix effects are operative.

9.4.2 The laboratory must add a known amount of each analyte to a minimum of 10% of the routine samples. In each case the LFM aliquot must be a duplicate of the aliquot used for sample analysis and for total recoverable determinations added prior to sample preparation. For water samples, the added analyte concentration must be the same as that used in the laboratory fortified blank (Section 7.10.3). For solid samples, however, the concentration added should be expressed as mg/kg and is calculated for a one gram aliquot by multiplying the added analyte concentration (mg/L) in solution by the conversion factor 100 (mg/L x 0.1L/0.001kg = 100, Section 12.5). (For notes on Ag,

Ba, and Sn see Sections 1.7 and 1.8.) Over time, samples from all routine sample sources should be fortified.

Note: The concentration of calcium, magnesium, sodium and strontium in environmental waters, along with iron and aluminum in solids can vary greatly and are not necessarily predictable. Fortifying these analytes in routine samples at the same concentration used for the LFB may prove to be of little use in assessing data quality for these analytes. For these analytes sample dilution and reanalysis using the criteria given in Section 9.5.2 is recommended. Also, if specified by the data user, laboratory or program, samples can be fortified at higher concentrations, but even major constituents should be limited to <25 mg/L so as not to alter the sample matrix and affect the analysis.

9.4.3 Calculate the percent recovery for each analyte, corrected for background concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range of 70-130% or a 3-sigma recovery range calculated from the regression equations given in Table 9.[16] Recovery calculations are not required if the concentration added is less than 30% of the sample background concentration. Percent recovery may be calculated in units appropriate to the matrix, using the following equation:

$$R = \frac{C_s - C}{s} X\ 100$$

Where:

R = percent recovery
C_s = fortified sample concentration
C = sample background concentration
s = concentration equivalent of analyte added to fortify the sample

9.4.4 If the recovery of any analyte falls outside the designated LFM recovery range, and the laboratory performance for that analyte is shown to be in control (Section 9.3), the recovery problem encountered with the fortified sample is judged to be matrix related, not system related. The data user should be informed that the result for that analyte in the unfortified sample is suspect due to either the heterogeneous nature of the sample or matrix effects and analysis by method of standard addition or the use of an internal standard(s) (Section 11.5) should be considered.

9.4.5 Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method

acceptably. Reference materials containing high concentrations of analytes can provide additional information on the performance of the spectral interference correction routine.

9.5 Assess the possible need for the method of standard additions (MSA) or internal standard elements by the following tests. Directions for using MSA or internal standard(s) are given in Section 11.5.

9.5.1 Analyte addition test: An analyte(s) standard added to a portion of a prepared sample, or its dilution, should be recovered to within 85% to 115% of the known value. The analyte(s) addition should produce a minimum level of 20 times and a maximum of 100 times the method detection limit. If the analyte addition is <20% of the sample analyte concentration, the following dilution test should be used. If recovery of the analyte(s) is not within the specified limits, a matrix effect should be suspected, and the associated data flagged accordingly. The method of additions or the use of an appropriate internal standard element may provide more accurate data.

9.5.2 Dilution test: If the analyte concentration is sufficiently high (minimally, a factor of 50 above the instrument detection limit in the original solution but <90% of the linear limit), an analysis of a 1+4 dilution should agree (after correction for the fivefold dilution) within ±10% of the original determination. If not, a chemical or physical interference effect should be suspected and the associated data flagged accordingly. The method of standard additions or the use of an internal-standard element may provide more accurate data for samples failing this test.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. However, because of the difference among various makes and models of spectrometers, specific instrument operating conditions cannot be given. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a task. Operating conditions for aqueous solutions usually vary from 1100-1200 watts forward power, 15-16 mm viewing height, 15-19 L/min. argon coolant flow, 0.6-1 L/min. argon aerosol flow, 1-1.8 mL/min. sample pumping rate with a one minute preflush time and measurement time near 1 s per wavelength peak (for sequential instruments) and near 10 s per sample (for simultaneous instruments). Use of the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm (by adjusting the argon aerosol flow) has been recommended as a way to achieve repeatable interference correction factors.[17]

10.2 Prior to using this method optimize the plasma operating conditions. The following procedure is recommended for vertically configured plasmas. The purpose of plasma optimization is to provide a maximum signal-to-background ratio for the least sensitive element in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow rate greatly facilitates the procedure.

10.2.1 Ignite the plasma and select an appropriate incident rf power with minimum reflected power. Allow the instrument to become thermally stable before beginning. This usually requires at least 30 to 60 minutes of operation. While aspirating the 1000 µg/mL solution of yttrium (Section 7.8.32), follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5-20 mm above the top of the work coil.[18] Record the nebulizer gas flow rate or pressure setting for future reference.

10.2.2 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min. by aspirating a known volume calibration blank for a period of at least three minutes. Divide the spent volume by the aspiration time (in minutes) and record the uptake rate. Set the peristaltic pump to deliver the uptake rate in a steady even flow.

10.2.3 After horizontally aligning the plasma and/or optically profiling the spectrometer, use the selected instrument conditions from Sections 10.2.1 and 10.2.2, and aspirate the plasma solution (Section 7.15), containing 10 µg/mL each of As, Pb, Se and Tl. Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14-18 mm above the top of the work coil. (This region of the plasma is commonly referred to as the analytical zone.)[19] Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the largest intensity ratio for the least sensitive element of the four analytes. If more than one position provides the same ratio, select the position that provides the highest net intensity counts for the least sensitive element or accept a compromise position of the intensity ratios of all four analytes.

10.2.4 The instrument operating condition finally selected as being optimum should provide the lowest reliable instrument detection limits and method detection limits. Refer to Tables 1 and 4 for comparison of IDLs and MDLs, respectively.

10.2.5 If either the instrument operating conditions, such as incident power and/or nebulizer gas flow rate are changed, or a new torch injector tube having a different orifice i.d. is installed, the plasma and plasma viewing height should be reoptimized.

10.2.6 Before daily calibration and after the instrument warmup period, the nebulizer gas flow must be reset to the determined optimized flow. If a mass flow controller is being used, it should be reset to the recorded optimized flow rate. In order to maintain valid spectral interelement correction routines the nebulizer gas flow rate should be the same from day-to-day (<2% change). The change in signal intensity with a change in nebulizer gas flow rate for both "hard" (Pb 220.353 nm) and "soft" (Cu 324.754) lines is illustrated in Figure 1.

10.3 Before using the procedure (Section 11.0) to analyze samples, there must be data available documenting initial demonstration of performance. The required data and procedure is described in Section 9.2. This data must be generated using the same instrument operating conditions and calibration routine (Section 11.4) to be used for sample analysis. These documented data must be kept on file and be available for review by the data user.

10.4 After completing the initial demonstration of performance, but before analyzing samples, the laboratory must establish and initially verify an interelement spectral interference correction routine to be used during sample analysis. A general description concerning spectral interference and the analytical requirements for background correction and for correction of interelement spectral interference in particular are given in Section 4.1. To determine the appropriate location for background correction and to establish the interelement interference correction routine, repeated spectral scan about the analyte wavelength and repeated analyses of the single element solutions may be required. Criteria for determining an interelement spectral interference is an apparent positive or negative concentration on the analyte that is outside the 3-sigma control limits of the calibration blank for the analyte. (The upper-control limit is the analyte IDL.) Once established, the entire routine must be initially and periodically verified annually, or whenever there is a change in instrument operating conditions (Section 10.2.5). Only a portion of the correction routine must be verified more frequently or on a daily basis. Test criteria and required solutions are described in Section 7.13. Initial and periodic verification data of the routine should be kept on file. Special cases where on-going verification are required is described in Section 7.14.

11.0 PROCEDURE

11.1 Aqueous Sample Preparation - Dissolved Analytes

11.1.1 For the determination of dissolved analytes in ground and surface waters, pipet an aliquot (≥ 20 mL) of the filtered, acid preserved sample into a 50 mL polypropylene centrifuge tube. Add an appropriate volume of (1+1) nitric acid to adjust the acid concentration of the aliquot to approximate a 1% (v/v) nitric acid solution (e.g., add 0.4 mL (1+1) HNO_3 to a 20 mL aliquot of sample). Cap the tube and mix. The sample is now ready for analysis (Section 1.3). Allowance for sample

dilution should be made in the calculations. (If mercury is to be determined, a separate aliquot must be additionally acidified to contain 1% (v/v) HCl to match the signal response of mercury in the calibration standard and reduce memory interference effects. Section 1.9).

Note: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be treated using the procedure described in Sections 11.2.2 through 11.2.7 prior to analysis.

11.2 Aqueous Sample Preparation - Total Recoverable Analytes

11.2.1 For the "direct analysis" of total recoverable analytes in drinking water samples containing turbidity <1 NTU, treat an unfiltered acid preserved sample aliquot using the sample preparation procedure described in Section 11.1.1 while making allowance for sample dilution in the data calculation (Section 1.2). For the determination of total recoverable analytes in all other aqueous samples or for preconcentrating drinking water samples prior to analysis follow the procedure given in Sections 11.2.2 through 11.2.7.

11.2.2 For the determination of total recoverable analytes in aqueous samples (other than drinking water with <1 NTU turbidity), transfer a 100 mL (±1 mL) aliquot from a well mixed, acid preserved sample to a 250 mL Griffin beaker (Sections 1.2, 1.3, 1.6, 1.7, 1.8, and 1.9). (When necessary, smaller sample aliquot volumes may be used.)

Note: If the sample contains undissolved solids >1%, a well mixed, acid preserved aliquot containing no more than 1 g particulate material should be cautiously evaporated to near 10 mL and extracted using the acid-mixture procedure described in Sections 11.3.3 through 11.3.6.

11.2.3 Add 2 mL (1+1) nitric acid and 1.0 mL of (1+1) hydrochloric acid to the beaker containing the measured volume of sample. Place the beaker on the hot plate for solution evaporation. The hot plate should be located in a fume hood and previously adjusted to provide evaporation at a temperature of approximately but no higher than 85°C. (See the following note.) The beaker should be covered with an elevated watch glass or other necessary steps should be taken to prevent sample contamination from the fume hood environment.

Note: For proper heating adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85°C. (Once the beaker is covered with a watch glass the temperature of the water will rise to approximately 95°C.)

11.2.4 Reduce the volume of the sample aliquot to about 20 mL by gentle heating at 85°C. DO NOT BOIL. This step takes about two hours for a 100 mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL. (A spare beaker containing 20 mL of water can be used as a gauge.)

11.2.5 Cover the lip of the beaker with a watch glass to reduce additional evaporation and gently reflux the sample for 30 minutes. (Slight boiling may occur, but vigorous boiling must be avoided to prevent loss of the HCl-H_2O azeotrope.)

11.2.6 Allow the beaker to cool. Quantitatively transfer the sample solution to a 50 mL volumetric flask, make to volume with reagent water, stopper and mix.

11.2.7 Allow any undissolved material to settle overnight, or centrifuge a portion of the prepared sample until clear. (If after centrifuging or standing overnight the sample contains suspended solids that would clog the nebulizer, a portion of the sample may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.) The sample is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

11.3 Solid Sample Preparation - Total Recoverable Analytes

11.3.1 For the determination of total recoverable analytes in solid samples, mix the sample thoroughly and transfer a portion (>20 g) to tared weighing dish, weigh the sample and record the wet weight (WW). (For samples with <35% moisture a 20 g portion is sufficient. For samples with moisture >35% a larger aliquot 50-100 g is required.) Dry the sample to a constant weight at 60°C and record the dry weight (DW) for calculation of percent solids (Section 12.6). (The sample is dried at 60°C to prevent the loss of mercury and other possible volatile metallic compounds, to facilitate sieving, and to ready the sample for grinding.)

11.3.2 To achieve homogeneity, sieve the dried sample using a 5-mesh polypropylene sieve and grind in a mortar and pestle. (The sieve, mortar and pestle should be cleaned between samples.) From the dried, ground material weigh accurately a representative 1.0 ± 0.01 g aliquot (W) of the sample and transfer to a 250 mL Phillips beaker for acid extraction (Sections1.6, 1.7, 1.8, and 1.9).

11.3.3 To the beaker add 4 mL of (1+1) HNO_3 and 10 mL of (1+4) HCl. Cover the lip of the beaker with a watch glass. Place the beaker on a hot plate for reflux extraction of the analytes. The hot plate should be

located in a fume hood and previously adjusted to provide a reflux temperature of approximately 95°C. (See the following note.)

Note: For proper heating adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85°C. (Once the beaker is covered with a watch glass the temperature of the water will rise to approximately 95°C.) Also, a block digester capable of maintaining a temperature of 95°C and equipped with 250 mL constricted volumetric digestion tubes may be substituted for the hot plate and conical beakers in the extraction step.

11.3.4 Heat the sample and gently reflux for 30 minutes. Very slight boiling may occur, however vigorous boiling must be avoided to prevent loss of the HCl-H_2O azeotrope. Some solution evaporation will occur (3-4 mL).

11.3.5 Allow the sample to cool and quantitatively transfer the extract to a 100 mL volumetric flask. Dilute to volume with reagent water, stopper and mix.

11.3.6 Allow the sample extract solution to stand overnight to separate insoluble material or centrifuge a portion of the sample solution until clear. (If after centrifuging or standing overnight the extract solution contains suspended solids that would clog the nebulizer, a portion of the extract solution may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration.) The sample extract is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

11.4 Sample Analysis

11.4.1 Prior to daily calibration of the instrument inspect the sample introduction system including the nebulizer, torch, injector tube and uptake tubing for salt deposits, dirt and debris that would restrict solution flow and affect instrument performance. Clean the system when needed or on a daily basis.

11.4.2 Configure the instrument system to the selected power and operating conditions as determined in Sections 10.1 and 10.2.

11.4.3 The instrument must be allowed to become thermally stable before calibration and analyses. This usually requires at least 30 to 60 minutes of operation. After instrument warmup, complete any required optical profiling or alignment particular to the instrument.

11.4.4 For initial and daily operation calibrate the instrument according to the instrument manufacturer's recommended procedures, using mixed calibration standard solutions (Section 7.9) and the calibration blank (Section 7.10.1). A peristaltic pump must be used to introduce all solutions to the nebulizer. To allow equilibrium to be reached in the plasma, aspirate all solutions for 30 seconds after reaching the plasma before beginning integration of the background corrected signal to accumulate data. When possible, use the average value of replicate integration periods of the signal to be correlated to the analyte concentration. Flush the system with the rinse blank (Section 7.10.4) for a minimum of 60 seconds (Section 4.4) between each standard. The calibration line should consist of a minimum of a calibration blank and a high standard. Replicates of the blank and highest standard provide an optimal distribution of calibration standards to minimize the confidence band for a straight-line calibration in a response region with uniform variance.[20]

11.4.5 After completion of the initial requirements of this method (Sections 10.3 and 10.4), samples should be analyzed in the same operational manner used in the calibration routine with the rinse blank also being used between all sample solutions, LFBs, LFMs, and check solutions (Section 7.10.4).

11.4.6 During the analysis of samples, the laboratory must comply with the required quality control described in Sections 9.3 and 9.4. Only for the determination of dissolved analytes or the "direct analysis" of drinking water with turbidity of <1 NTU is the sample digestion step of the LRB, LFB, and LFM not required.

11.4.7 Determined sample analyte concentrations that are 90% or more of the upper limit of the analyte LDR must be diluted with reagent water that has been acidified in the same manner as calibration blank and reanalyzed (see Section 11.4.8). Also, for the interelement spectral interference correction routines to remain valid during sample analysis, the interferant concentration must not exceed its LDR. If the interferant LDR is exceeded, sample dilution with acidified reagent water and reanalysis is required. In these circumstances analyte detection limits are raised and determination by another approved test procedure that is either more sensitive and/or interference free is recommended.

11.4.8 When it is necessary to assess an operative matrix interference (e.g., signal reduction due to high dissolved solids), the tests described in Section 9.5 are recommended.

11.4.9 Report data as directed in Section 12.0.

11.5 If the method of standard additions (MSA) is used, standards are added at one or more levels to portions of a prepared sample. This technique[21] compensates

for enhancement or depression of an analyte signal by a matrix. It will not correct for additive interferences such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single-addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated by the following:

$$\text{Sample Conc. (mg/L or mg/kg)} = \frac{S_2 \times V_1 \times C}{(S_1 - S_2) \times V_2}$$

where:

C = Concentration of the standard solution (mg/L)
S_1 = Signal for fortified aliquot
S_2 = Signal for unfortified aliquot
V_1 = Volume of the standard addition (L)
V_2 = Volume of the sample aliquot (L) used for MSA

For more than one fortified portion of the prepared sample, linear regression analysis can be applied using a computer or calculator program to obtain the concentration of the sample solution. An alternative to using the method of standard additions is use of the internal standard technique by adding one or more elements (not in the samples and verified not to cause an uncorrected interelement spectral interference) at the same concentration (which is sufficient for optimum precision) to the prepared samples (blanks and standards) that are affected the same as the analytes by the sample matrix. Use the ratio of analyte signal to the internal standard signal for calibration and quantitation.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Sample data should be reported in units of mg/L for aqueous samples and mg/kg dry weight for solid samples.

12.2 For dissolved aqueous analytes (Section 11.1) report the data generated directly from the instrument with allowance for sample dilution. Do not report analyte concentrations below the IDL.

12.3 For total recoverable aqueous analytes (Section 11.2), multiply solution analyte concentrations by the dilution factor 0.5, when 100 mL aliquot is used to produce the 50 mL final solution, and report data as instructed in Section 12.4. If a different aliquot volume other than 100 mL is used for sample preparation,

adjust the dilution factor accordingly. Also, account for any additional dilution of the prepared sample solution needed to complete the determination of analytes exceeding 90% or more of the LDR upper limit. Do not report data below the determined analyte MDL concentration or below an adjusted detection limit reflecting smaller sample aliquots used in processing or additional dilutions required to complete the analysis.

12.4 For analytes with MDLs <0.01 mg/L, round the data values to the thousandth place and report analyte concentrations up to three significant figures. For analytes with MDLs ≥ 0.01 mg/L round the data values to the 100th place and report analyte concentrations up to three significant figures. Extract concentrations for solids data should be rounded in a similar manner before calculations in Section 12.5 are performed.

12.5 For total recoverable analytes in solid samples (Section 11.3), round the solution analyte concentrations (mg/L) as instructed in Section 12.4. Report the data up to three significant figures as mg/kg dry-weight basis unless specified otherwise by the program or data user. Calculate the concentration using the equation below:

$$\text{Sample Conc. (mg/kg) dry-weight basis} = \frac{C \times V \times D}{W}$$

where:

C = Concentration in extract (mg/L)
V = Volume of extract (L, 100 mL = 0.1L)
D = Dilution factor (undiluted = 1)
W = Weight of sample aliquot extracted (g x 0.001 = kg)

Do not report analyte data below the estimated solids MDL or an adjusted MDL because of additional dilutions required to complete the analysis.

12.6 To report percent solids in solid samples (Section 11.3) calculate as follows:

$$\% \text{ solids (S)} = \frac{DW}{WW} \times 100$$

where:

DW = Sample weight (g) dried at 60°C
WW = Sample weight (g) before drying

Note: If the data user, program or laboratory requires that the reported percent solids be determined by drying at 105°C, repeat the procedure given in

Section 11.3 using a separate portion (>20 g) of the sample and dry to constant weight at 103-105°C.

12.7 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.

13.0 METHOD PERFORMANCE

13.1 Listed in Table 4 are typical single laboratory total recoverable MDLs determined for the recommended wavelengths using simultaneous ICP-AES and the operating conditions given in Table 5. The MDLs were determined in reagent blank matrix (best case situation). PTFE beakers were used to avoid boron and silica contamination from glassware with the final dilution to 50 mL completed in polypropylene centrifuged tubes. The listed MDLs for solids are estimates and were calculated from the aqueous MDL determinations.

13.2 Data obtained from single laboratory method testing are summarized in Table 6 for five types of water samples consisting of drinking water, surface water, ground water, and two wastewater effluents. The data presented cover all analytes except cerium and titanium. Samples were prepared using the procedure described in Section 11.2. For each matrix, five replicate aliquots were prepared, analyzed and the average of the five determinations used to define the sample background concentration of each analyte. In addition, two pairs of duplicates were fortified at different concentration levels. For each method analyte, the sample background concentration, mean percent recovery, standard deviation of the percent recovery, and relative percent difference between the duplicate fortified samples are listed in Table 6. The variance of the five replicate sample background determinations is included in the calculated standard deviation of the percent recovery when the analyte concentration in the sample was greater than the MDL. The tap and well waters were processed in Teflon and quartz beakers and diluted in polypropylene centrifuged tubes. The nonuse of borosilicate glassware is reflected in the precision and recovery data for boron and silica in those two sample types.

13.3 Data obtained from single laboratory method testing are summarized in Table 7 for three solid samples consisting of EPA 884 Hazardous Soil, SRM 1645 River Sediment, and EPA 286 Electroplating Sludge. Samples were prepared using the procedure described in Section 11.3. For each method analyte, the sample background concentration, mean percent recovery of the fortified additions, the standard deviation of the percent recovery, and relative percent difference between duplicate additions were determined as described in Section 13.2. Data presented are for all analytes except cerium, silica, and titanium. Limited comparative data to other methods and SRM materials are presented in Reference 23 of Section 16.0.

13.4 Performance data for aqueous solutions independent of sample preparation from a multilaboratory study are provided in Table 8.[22]

13.5 Listed in Table 9 are regression equations for precision and bias for 25 analytes abstracted from EPA Method Study 27, a multilaboratory validation study of Method 200.7.[1] These equations were developed from data received from 12 laboratories using the total recoverable sample preparation procedure on reagent water, drinking water, surface water and three industrial effluents. For a complete review and description of the study. See Reference 16 of Section 16.0.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous 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 (e.g., Section 7.8). When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable 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 N.W., Washington D.C. 20036, (202)872-4477.

15.0 WASTE MANAGEMENT

15.1 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 the Section 14.2.

16.0 REFERENCES

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17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1: WAVELENGTHS, ESTIMATED INSTRUMENT DETECTION LIMITS, AND RECOMMENDED CALIBRATION

Analyte	Wavelength[a] (nm)	Estimated Detection Limit[b] (µg/L)	Calibrate[c] to (mg/L)
Aluminum	308.215	45	10
Antimony	206.833	32	5
Arsenic	193.759	53	10
Barium	493.409	2.3	1
Beryllium	313.042	0.27	1
Boron	249.678	5.7	1
Cadmium	226.502	3.4	2
Calcium	315.887	30	10
Cerium	413.765	48	2
Chromium	205.552	6.1	5
Cobalt	228.616	7.0	2
Copper	324.754	5.4	2
Iron	259.940	6.2	10
Lead	220.353	42	10
Lithium	670.784	3.7[d]	5
Magnesium	279.079	30	10
Manganese	257.610	1.4	2
Mercury	194.227	2.5	2
Molybdenum	203.844	12	10
Nickel	231.604	15	2
Phosphorus	214.914	76	10
Potassium	766.491	700[e]	20
Selenium	196.090	75	5
Silica (SiO_2)	251.611	26[d] (SiO_2)	10
Silver	328.068	7.0	0.5
Sodium	588.995	29	10
Strontium	421.552	0.77	1
Thallium	190.864	40	5
Tin	189.980	25	4
Titanium	334.941	3.8	10
Vanadium	292.402	7.5	2
Zinc	213.856	1.8	5

[a]The wavelengths listed are recommended because of their sensitivity and overall acceptability. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Section 4.1).

[b]These estimated 3-sigma instrumental detection limits[16] are provided only as a guide to instrumental limits. The method detection limits are sample dependent and may vary as the sample matrix varies. Detection limits for solids can be estimated by dividing these values by the grams extracted per liter, which depends upon the extraction procedure. Divide solution detection limits by 10 for 1 g extracted to 100 mL for solid detection limits.

[c]Suggested concentration for instrument calibration[2]. Other calibration limits in the linear ranges may be used.

[d]Calculated from 2-sigma data[5].

[e]Highly dependent on operating conditions and plasma position.

TABLE 2: ON-LINE METHOD INTERELEMENT SPECTRAL INTERFERANCES ARISING FROM INTERFERANTS AT THE 100 mg/L LEVEL

Analyte	Wavelength (nm)	Interferant*
Ag	328.068	Ce, Ti, Mn
Al	308.215	V, Mo, Ce, Mn
As	193.759	V, Al, Co, Fe, Ni
B	249.678	None
Ba	493.409	None
Be	313.042	V, Ce
Ca	315.887	Co, Mo, Ce
Cd	226.502	Ni, Ti, Fe, Ce
Ce	413.765	None
Co	228.616	Ti, Ba, Cd, Ni, Cr, Mo, Ce
Cr	205.552	Be, Mo, Ni
Cu	324.754	Mo, Ti
Fe	259.940	None
Hg	194.227	V, Mo
K	766.491	None
Li	670.784	None
Mg	279.079	Ce
Mn	257.610	Ce
Mo	203.844	Ce
Na	588.995	None
Ni	231.604	Co, Tl
P	214.914	Cu, Mo
Pb	220.353	Co, Al, Ce, Cu, Ni, Ti, Fe
Sb	206.833	Cr, Mo, Sn, Ti, Ce, Fe
Se	196.099	Fe
SiO_2	251.611	None
Sn	189.980	Mo, Ti, Fe, Mn, Si
Sr	421.552	None
Tl	190.864	Ti, Mo, Co, Ce, Al, V, Mn
Ti	334.941	None
V	292.402	Mo, Ti, Cr, Fe, Ce
Zn	213.856	Ni, Cu, Fe

*These on-line interferences from method analytes and titanium only were observed using an instrument with 0.035 nm resolution (see Section 4.1.2). Interferant ranked by magnitude of intensity with the most severe interferant listed first in the row.

TABLE 3: MIXED STANDARD SOLUTIONS

Solution	Analytes
I	Ag, As, B, Ba, Ca, Cd, Cu, Mn, Sb, and Se
II	K, Li, Mo, Na, Sr, and Ti
III	Co, P, V, and Ce
IV	Al, Cr, Hg, SiO_2, Sn, and Zn
V	Be, Fe, Mg, Ni, Pb, and Tl

TABLE 4: TOTAL RECOVERABLE METHOD DETECTION LIMITS (MDL)

	MDLs	
Analyte	**Aqueous, mg/L[1])**	**Solids, mg/kg[2])**
Ag	0.002	0.3
Al	0.02	3
As	0.008	2
B	0.003	–
Ba	0.001	0.2
Be	0.0003	0.1
Ca	0.01	2
Cd	0.001	0.2
Ce	0.02	3
Co	0.002	0.4
Cr	0.004	0.8
Cu	0.003	0.5
Fe	0.03*	6
Hg	0.007	2
K	0.3	60
Li	0.001	0.2
Mg	0.02	3
Mn	0.001	0.2
Mo	0.004	1
Na	0.03	6
Ni	0.005	1
P	0.06	12
Pb	0.01	2
Sb	0.008	2
Se	0.02	5
SiO_2	0.02	–
Sn	0.007	2
Sr	0.0003	0.1
Tl	0.001	0.2
Ti	0.02	3
V	0.003	1
Zn	0.002	0.3

[1] MDL concentrations are computed for original matrix with allowance for 2x sample preconcentration during preparation. Samples were processed in PTFE and diluted in 50-mL plastic centrifuge tubes.

[2] Estimated, calculated from aqueous MDL determinations.

– Boron not reported because of glassware contamination. Silica not determined in solid samples.

* Elevated value due to fume-hood contamination.

TABLE 5: INDUCTIVELY COUPLED PLASMA INSTRUMENT OPERATING CONDITIONS

Incident rf power	1100 watts
Reflected rf power	<5 watts
Viewing height above work coil	15 mm
Injector tube orifice i.d.	1 mm
Argon supply	liquid argon
Argon pressure	40 psi
Coolant argon flow rate	19 L/min.
Aerosol carrier argon flow rate	620 mL/min.
Auxiliary (plasma) argon flow rate	300 mL/min.
Sample uptake rate controlled to	1.2 mL/min.

TABLE 6: PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES

TAP WATER

Analyte	Sample Conc. mg/L	Low Spike mg/L	Average Recovery R (%)	S (R)	RPD	High Spike mg/L	Average Recovery R (%)	S (R)	RPD
Ag	<0.002	0.05	95	0.7	2.1	0.2	96	0.0	0.0
Al	0.185	0.05	98	8.8	1.7	0.2	105	3.0	3.1
As	<0.008	0.05	108	1.4	3.7	0.2	101	0.7	2.0
B	0.023	0.1	98	0.2	0.0	0.4	98	0.2	0.5
Ba	0.042	0.05	102	1.6	2.2	0.2	98	0.4	0.8
Be	<0.0003	0.01	100	0.0	0.0	0.1	99	0.0	0.0
Ca	35.2	5.0	101	8.8	1.7	20.0	103	2.0	0.9
Cd	<0.001	0.01	105	3.5	9.5	0.1	98	0.0	0.0
Co	<0.002	0.02	100	0.0	0.0	0.2	99	0.5	1.5
Cr	<0.004	0.01	110	0.0	0.0	0.1	102	0.0	0.0
Cu	<0.003	0.02	103	1.8	4.9	0.2	101	1.2	3.5
Fe	0.008	0.1	106	1.0	1.8	0.4	105	0.3	0.5
Hg	<0.007	0.05	103	0.7	1.9	0.2	100	0.4	1.0
K	1.98	5.0	109	1.4	2.3	20.	107	0.7	1.7
Li	0.006	0.02	103	6.9	3.8	0.2	110	1.9	4.4
Mg	8.08	5.0	104	2.2	1.5	20.0	100	0.7	1.1
Mn	<0.001	0.01	100	0.0	0.0	0.1	99	0.0	0.0
Mo	<0.004	0.02	95	3.5	10.5	0.2	108	0.5	1.4
Na	10.3	5.0	99	3.0	2.0	20.0	106	1.0	1.6
Ni	<0.005	0.02	108	1.8	4.7	0.2	104	1.1	2.9
P	0.045	0.1	102	13.1	9.4	0.4	104	3.2	1.3
Pb	<0.01	0.05	95	0.7	2.1	0.2	100	0.2	0.5
Sb	<0.008	0.05	99	0.7	2.0	0.2	102	0.7	2.0
Se	<0.02	0.1	87	1.1	3.5	0.4	99	0.8	2.3
SiO_2	6.5	5.0	104	3.3	3.4	20.0	96	1.1	2.3
Sn	<0.007	0.05	103	2.1	5.8	0.2	101	1.8	5.0
Sr	0.181	0.1	102	3.3	2.1	0.4	105	0.8	1.0
Tl	<0.02	0.1	101	3.9	10.9	0.4	101	0.1	0.3
V	<0.003	0.05	101	0.7	2.0	0.2	99	0.2	0.5
Zn	0.005	0.05	101	3.7	9.0	0.2	98	0.9	2.5

S (R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 6: PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont'd)

POND WATER

Analyte	Sample Conc. mg/L	Low Spike mg/L	Average Recovery R (%)	S (R)	RPD	High Spike mg/L	Average Recovery R (%)	S (R)	RPD
Ag	<0.002	0.05	92	0.0	0.0	0.2	94	0.0	0.0
Al	0.819	0.2	88	10.0	5.0	0.8	100	2.9	3.7
As	<0.008	0.05	102	0.0	0.0	0.2	98	1.4	4.1
B	0.034	0.1	111	8.9	6.9	0.4	103	2.0	0.0
Ba	0.029	0.05	96	0.9	0.0	0.2	97	0.3	0.5
Be	<0.0003	0.01	95	0.4	1.1	0.2	95	0.0	0.0
Ca	53.9	5.0	*	*	0.7	20.0	100	2.0	1.5
Cd	<0.001	0.01	107	0.0	0.0	0.1	97	0.0	0.0
Co	<0.002	0.02	100	2.7	7.5	0.2	97	0.7	2.1
Cr	<0.004	0.01	105	3.5	9.5	0.1	103	1.1	2.9
Cu	<0.003	0.02	98	2.1	4.4	0.2	100	0.5	1.5
Fe	0.875	0.2	95	8.9	2.8	0.8	97	3.2	3.6
Hg	<0.007	0.05	97	3.5	10.3	0.2	98	0.0	0.0
K	2.48	5.0	106	0.3	0.1	20.0	103	0.2	0.4
Li	<0.001	0.02	110	0.0	0.0	0.2	106	0.2	0.5
Mg	10.8	5.0	102	0.5	0.0	20.0	96	0.7	1.3
Mn	0.632	0.01	*	*	0.2	0.1	97	2.3	0.3
Mo	<0.004	0.02	105	3.5	9.5	0.2	103	0.4	1.0
Na	17.8	5.0	103	1.3	0.4	20.0	94	0.3	0.0
Ni	<0.005	0.02	96	5.6	9.1	0.2	100	0.7	1.5
P	0.196	0.1	91	14.7	0.3	0.4	108	3.9	1.3
Pb	<0.01	0.05	96	2.6	7.8	0.2	100	0.7	2.0
Sb	<0.008	0.05	102	2.8	7.8	0.2	104	0.4	1.0
Se	<0.02	0.1	104	2.1	5.8	0.4	103	1.6	4.4
SiO_2	7.83	5.0	151	1.6	1.3	20.0	117	0.4	0.6
Sn	<0.007	0.05	98	0.0	0.0	0.2	99	1.1	3.0
Sr	0.129	0.1	105	0.4	0.0	0.4	99	0.1	0.2
Tl	<0.02	0.1	103	1.1	2.9	0.4	97	1.3	3.9
V	0.003	0.05	94	0.4	0.0	0.2	98	0.1	0.0
Zn	0.006	0.05	97	1.6	1.8	0.2	94	0.4	0.0

S (R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 6: PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont'd)

WELL WATER

Analyte	Sample Conc. mg/L	Low Spike mg/L	Average Recovery R (%)	S (R)	RPD	High Spike mg/L	Average Recovery R (%)	S (R)	RPD
Ag	<0.002	0.05	97	0.7	2.1	0.2	96	0.2	0.5
Al	0.036	0.05	107	7.6	10.1	0.2	101	1.1	0.8
As	<0.008	0.05	107	0.7	1.9	0.2	104	0.4	1.0
B	0.063	0.1	97	0.6	0.7	0.4	98	0.8	2.1
Ba	0.102	0.05	102	3.0	0.0	0.2	99	0.9	1.0
Be	<0.0003	0.01	100	0.0	0.0	0.1	100	0.0	0.0
Ca	93.8	5.0	*	*	2.1	20.0	100	4.1	0.1
Cd	0.002	0.01	90	0.0	0.0	0.1	96	0.0	0.0
Co	<0.002	0.02	94	0.4	1.1	0.2	94	0.4	1.1
Cr	<0.004	0.01	100	7.1	20.0	0.1	100	0.4	1.0
Cu	<0.005	0.02	100	1.1	0.4	0.2	96	0.5	1.5
Fe	0.042	0.1	99	2.3	1.4	0.4	97	1.4	3.3
Hg	<0.007	0.05	94	2.8	8.5	0.2	93	1.2	3.8
K	6.21	5.0	96	3.4	3.6	20.0	101	1.2	2.3
Li	0.001	0.02	100	7.6	9.5	0.2	104	1.0	1.9
Mg	24.5	5.0	95	5.6	0.3	20.0	93	1.6	1.2
Mn	2.76	0.01	*	*	0.4	0.1	*	*	0.7
Mo	<0.004	0.02	108	1.8	4.7	0.2	101	0.2	0.5
Na	35.0	5.0	101	11.4	0.8	20.0	100	3.1	1.5
Ni	<0.005	0.02	112	1.8	4.4	0.2	96	0.2	0.5
P	0.197	0.1	95	12.7	1.9	0.4	98	3.4	0.9
Pb	<0.01	0.05	87	4.9	16.1	0.2	95	0.2	0.5
Sb	<0.008	0.05	98	2.8	8.2	0.2	99	1.4	4.0
Se	<0.02	0.1	102	0.4	1.0	0.4	94	1.1	3.4
SiO_2	13.1	5.0	93	4.8	2.8	20.0	99	0.8	0.0
Sn	<0.007	0.05	98	2.8	8.2	0.2	94	0.2	0.5
Sr	0.274	0.1	94	5.7	2.7	0.4	95	1.7	2.2
Tl	<0.02	0.1	92	0.4	1.1	0.4	95	1.1	3.2
V	<0.003	0.05	98	0.0	0.0	0.2	99	0.4	1.0
Zn	0.538	0.05	*	*	0.7	0.2	99	2.5	1.1

S (R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 6: PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont'd)

SEWAGE TREATMENT PRIMARY EFFLUENT

Analyte	Sample Conc. mg/L	Low Spike mg/L	Average Recovery R (%)	S (R)	RPD	High Spike mg/L	Average Recovery R (%)	S (R)	RPD
Ag	0.009	0.05	92	1.5	3.6	0.2	95	0.1	0.0
Al	1.19	0.05	*	*	0.9	0.2	113	12.4	2.1
As	<0.008	0.05	99	2.1	6.1	0.2	93	2.1	6.5
B	0.226	0.1	217	16.3	9.5	0.4	119	13.1	20.9
Ba	0.189	0.05	90	6.8	1.7	0.2	99	1.6	0.5
Be	<0.0003	0.01	94	0.4	1.1	0.1	100	0.4	1.0
Ca	87.9	5.0	*	*	0.6	20.0	101	3.7	0.0
Cd	0.009	0.01	89	2.6	2.3	0.1	97	0.4	1.0
Co	0.016	0.02	95	3.1	0.0	0.2	93	0.4	0.5
Cr	0.128	0.01	*	*	1.5	0.1	97	2.4	2.7
Cu	0.174	0.02	98	33.1	4.7	0.2	98	3.0	1.4
Fe	1.28	0.1	*	*	2.8	0.4	111	7.0	0.6
Hg	<0.007	0.05	102	1.4	3.9	0.2	98	0.5	1.5
K	10.6	5.0	104	2.8	1.3	20.0	101	0.6	0.0
Li	0.011	0.02	103	8.5	3.2	0.2	105	0.8	0.5
Mg	22.7	5.0	100	4.4	0.0	20.0	92	1.1	0.2
Mn	0.199	0.01	*	*	2.0	0.1	104	1.9	0.3
Mo	0.125	0.02	110	21.2	6.8	0.2	102	1.3	0.9
Na	0.236	5.0	*	*	0.0	20.0	*	*	0.4
Ni	0.087	0.02	122	10.7	4.5	0.2	98	0.8	1.1
P	4.71	0.1	*	*	2.6	0.4	*	*	1.4
Pb	0.015	0.05	91	3.5	5.0	0.2	96	1.3	2.9
Sb	<0.008	0.05	97	0.7	2.1	0.2	103	1.1	2.9
Se	<0.02	0.1	108	3.9	10.0	0.4	101	2.6	7.2
SiO_2	16.7	5.0	124	4.0	0.9	20.0	108	1.1	0.8
Sn	0.016	0.05	90	3.8	0.0	0.2	95	1.0	0.0
Sr	0.515	0.1	103	6.4	0.5	0.4	96	1.6	0.2
Tl	<0.02	0.1	105	0.4	1.0	0.4	95	0.0	0.0
V	0.003	0.05	93	0.9	2.0	0.2	97	0.2	0.5
Zn	0.160	0.05	98	3.3	1.9	0.2	101	1.0	1.4

S (R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 6: PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont'd)

INDUSTRIAL EFFLUENT

Analyte	Sample Conc. mg/L	Low Spike mg/L	Average Recovery R (%)	S (R)	RPD	High Spike mg/L	Average Recovery R (%)	S (R)	RPD
Ag	<0.0003	0.05	88	0.0	0.0	0.2	84	0.9	3.0
Al	0.054	0.05	88	11.7	12.2	0.2	90	3.9	8.1
As	<0.02	0.05	82	2.8	9.8	0.2	88	0.5	1.7
B	0.17	0.1	162	17.6	13.9	0.4	92	4.7	9.3
Ba	0.083	0.05	86	8.2	1.6	0.2	85	2.3	2.4
Be	<0.0006	0.01	94	0.4	1.1	0.1	82	1.4	4.9
Ca	500	5.0	*	*	2.8	20.0	*	*	2.3
Cd	0.008	0.01	85	4.7	6.1	0.1	82	1.4	4.4
Co	<0.004	0.02	93	1.8	5.4	0.2	83	0.4	1.2
Cr	0.165	0.01	*	*	4.5	0.1	106	6.6	5.6
Cu	0.095	0.02	93	23.3	0.9	0.2	95	2.7	2.8
Fe	0.315	0.1	88	16.4	1.0	0.4	99	6.5	8.0
Hg	<0.01	0.05	87	0.7	2.3	0.2	86	0.4	1.2
K	2.87	5.0	101	3.4	2.4	20.0	100	0.8	0.4
Li	0.069	0.02	103	24.7	5.6	0.2	104	2.5	2.2
Mg	6.84	5.0	87	3.1	0.0	20.0	87	0.9	1.2
Mn	0.141	0.01	*	*	1.2	0.1	89	6.6	4.8
Mo	1.27	0.02	*	*	0.0	0.2	100	15.0	2.7
Na	1500	5.0	*	*	2.7	20.0	*	*	2.0
Ni	0.014	0.02	98	4.4	3.0	0.2	87	0.5	1.1
P	0.326	0.1	105	16.0	4.7	0.4	97	3.9	1.4
Pb	0.251	0.05	80	19.9	1.4	0.2	88	5.0	0.9
Sb	2.81	0.05	*	*	0.4	0.2	*	*	2.0
Se	0.021	0.1	106	2.6	3.2	0.4	105	1.9	4.6
SiO_2	6.83	5.0	99	6.8	1.7	20.0	100	2.2	3.0
Sn	<0.01	0.05	87	0.7	2.3	0.2	86	0.4	1.2
Sr	6.54	0.1	*	*	2.0	0.4	*	*	2.7
Tl	<0.03	0.1	87	1.8	5.8	0.4	84	1.1	3.6
V	<0.005	0.05	90	1.4	4.4	0.2	84	1.1	3.6
Zn	0.024	0.05	89	6.0	4.4	0.2	91	3.5	8.9

S (R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.

TABLE 7: PRECISION AND RECOVERY DATA IN SOLID MATRICES

EPA HAZARDOUS SOIL #884

Analyte	Sample Conc. mg/kg	Low+ Spike mg/kg	Average Recovery R (%)	S (R)	RPD	High+ Spike mg/kg	Average Recovery R (%)	S (R)	RPD
Ag	1.1	20	98	0.7	1.0	100	96	0.2	0.6
Al	5080	20	*	*	7.2	100	*	*	5.4
As	5.7	20	95	5.4	10.6	100	96	1.4	3.6
B	20.4	100	93	2.7	5.3	400	100	2.1	5.5
Ba	111	20	98	71.4	22.2	100	97	10.0	1.0
Be	0.66	20	97	0.7	2.3	100	99	0.1	0.2
Ca	85200	–	–	–	–	–	–	–	–
Cd	2	20	93	0.7	1.0	100	94	0.2	0.4
Co	5.5	20	96	3.5	7.7	100	93	0.8	2.1
Cr	79.7	20	87	28.8	16.5	100	104	1.3	1.1
Cu	113	20	110	16.2	4.4	100	104	4.0	4.2
Fe	16500	–	–	–	–	–	–	–	–
Hg	<1.4	10	92	2.5	7.7	40	98	0.0	0.0
K	621	500	121	1.3	0.0	2000	107	0.9	1.8
Li	6.7	10	113	3.5	4.4	40	106	0.6	0.6
Mg	24400	500	*	*	8.4	2000	*	*	10.1
Mn	343	20	*	*	8.5	100	95	11.0	1.6
Mo	5.3	20	88	5.3	13.2	100	91	1.4	4.1
Na	195	500	102	2.2	2.4	2000	100	1.5	3.7
Ni	15.6	20	100	1.8	0.0	100	94	1.5	3.6
P	595	500	106	13.4	8.0	2000	103	3.2	2.7
Pb	145	20	88	51.8	17.9	100	108	15.6	17.4
Sb	6.1	20	83	3.9	7.5	100	81	1.9	5.9
Se	<5	20	79	14.7	52.4	100	99	0.7	2.1
Sn	16.6	20	91	34.6	5.8	80	112	8.7	2.8
Sr	102	100	84	9.6	10.8	400	94	2.5	4.6
Tl	<4	20	92	4.8	14.6	100	91	1.5	4.6
V	16.7	20	104	4.2	5.4	100	99	0.8	1.7
Zn	131	20	103	31.2	7.3	100	104	7.2	6.4

S (R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
– Not spiked.
+ Equivalent.

TABLE 7: PRECISION AND RECOVERY DATA IN SOLID MATRICES (Cont'd)

EPA ELECTROPLATING SLUDGE #286

Analyte	Sample Conc. mg/kg	Low+ Spike mg/kg	Average Recovery R (%)	S (R)	RPD	High+ Spike mg/kg	Average Recovery R (%)	S (R)	RPD
Ag	6	20	96	0.2	0.4	100	93	0.1	0.4
Al	4980	20	*	*	4.4	100	*	*	5.6
As	32	20	94	1.3	0.8	100	97	0.7	1.6
B	210	100	113	2.0	1.6	400	98	1.9	3.5
Ba	39.8	20	0	6.8	0.3	100	0	1.6	5.7
Be	0.32	20	96	0.2	0.5	100	101	0.7	2.0
Ca	48500	–	–	–	–	–	–	–	–
Cd	108	20	98	2.5	0.8	100	96	0.5	0.5
Co	5.9	20	93	2.9	5.7	100	93	0.6	1.5
Cr	7580	20	*	*	0.7	100	*	*	1.3
Cu	806	20	*	*	1.5	100	94	8.3	0.7
Fe	31100	–	–	–	–	–	–	–	–
Hg	6.1	10	90	2.5	4.0	40	97	1.7	4.3
K	2390	500	75	8.3	4.0	2000	94	2.9	3.8
Li	9.1	10	101	2.8	0.5	40	106	1.6	3.1
Mg	1950	500	110	2.0	0.8	2000	108	2.3	3.2
Mn	262	20	*	*	1.8	100	91	1.2	0.9
Mo	13.2	20	92	2.1	2.9	100	92	0.3	0.0
Na	73400	500	*	*	1.7	2000	*	*	1.4
Ni	456	20	*	*	0.4	100	88	2.7	0.9
P	9610	500	*	*	2.9	2000	114	7.4	3.4
Pb	1420	20	*	*	2.1	100	*	*	1.3
Sb	<2	20	76	0.9	3.3	100	75	2.8	10.7
Se	6.3	20	86	9.0	16.6	100	103	1.6	2.7
Sn	24.0	20	87	4.0	2.7	80	92	0.7	0.0
Sr	145	100	90	8.1	8.1	400	93	2.4	4.6
Tl	16	20	89	4.6	5.3	100	92	0.8	0.9
V	21.7	20	95	1.2	1.0	100	96	0.4	0.9
Zn	12500	20	*	*	0.8	100	*	*	0.8

S (R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
– Not spiked.
+ Equivalent.

TABLE 7: PRECISION AND RECOVERY DATA IN SOLID MATRICES (Cont'd)

NBS 1645 RIVER SEDIMENT

Analyte	Sample Conc. mg/kg	Low+ Spike mg/kg	Average Recovery R (%)	S (R)	RPD	High+ Spike mg/kg	Average Recovery R (%)	S (R)	RPD
Ag	1.6	20	92	0.4	1.0	100	96	0.3	0.9
Al	5160	20	*	*	8.4	100	*	*	2.4
As	62.8	20	89	14.4	9.7	100	97	2.9	5.0
B	31.9	100	116	7.1	13.5	400	95	0.6	1.5
Ba	54.8	20	95	6.1	2.8	100	98	1.2	1.3
Be	0.72	20	101	0.4	1.0	100	103	1.4	3.9
Ca	28000	–	–	–	–	–	–	–	–
Cd	9.7	20	100	1.1	0.0	100	101	0.7	1.8
Co	9.4	20	98	3.8	4.8	100	98	0.9	1.8
Cr	28500	20	*	*	0.4	100	*	*	0.7
Cu	109	20	115	8.5	0.0	100	102	1.8	1.0
Fe	84800	–	–	–	–	–	–	–	–
Hg	3.1	10	99	4.3	7.7	40	96	0.7	1.0
K	452	500	98	4.1	2.0	2000	106	1.4	2.3
Li	3.7	10	101	2.0	0.7	40	108	1.3	3.0
Mg	6360	500	*	*	1.8	2000	93	2.7	1.0
Mn	728	20	*	*	3.5	100	97	12.4	2.2
Mo	17.9	20	97	12.5	18.5	100	98	0.6	0.0
Na	1020	500	92	2.6	0.0	2000	97	1.1	1.7
Ni	36.2	20	94	5.9	4.0	100	100	1.1	1.5
P	553	500	102	1.4	0.9	2000	100	0.8	1.6
Pb	707	20	*	*	0.8	100	103	5.9	0.4
Sb	22.8	20	86	2.3	0.0	100	88	0.6	0.9
Se	6.7	20	103	14.3	27.1	100	98	3.1	7.6
Sn	309	20	*	*	1.0	80	101	7.9	2.7
Sr	782	100	91	12.3	3.0	400	96	3.3	2.6
Tl	<4	20	90	0.0	0.0	100	95	1.3	4.0
V	20.1	20	89	5.4	5.8	100	98	0.7	0.0
Zn	1640	20	*	*	1.8	100	*	*	1.1

S (R) Standard deviation of percent recovery.
RPD Relative percent difference between duplicate spike determinations.
< Sample concentration below established method detection limit.
* Spike concentration <10% of sample background concentration.
– Not spiked.
+ Equivalent.

TABLE 8: ICP-AES INSTRUMENTAL PRECISION AND ACCURACY FOR AQUEOUS SOLUTIONS[a]

Element	Mean Conc. (mg/L)	N[b]	RSD (%)	Accuracy[c] (% of Nominal)
Al	14.8	8	6.3	100
Sb	15.1	8	7.7	102
As	14.7	7	6.4	99
Ba	3.66	7	3.1	99
Be	3.78	8	5.8	102
Cd	3.61	8	7.0	97
Ca	15.0	8	7.4	101
Cr	3.75	8	8.2	101
Co	3.52	8	5.9	95
Cu	3.58	8	5.6	97
Fe	14.8	8	5.9	100
Pb	14.4	7	5.9	97
Mg	14.1	8	6.5	96
Mn	3.70	8	4.3	100
Mo	3.70	8	6.9	100
Ni	3.70	7	5.7	100
K	14.1	8	6.6	95
Se	15.3	8	7.5	104
Na	14.0	8	4.2	95
Tl	15.1	7	8.5	102
V	3.51	8	6.6	95
Zn	3.57	8	8.3	96

[a]These performance values are independent of sample preparation because the labs analyzed portions of the same solutions using sequential or simultaneous instruments.[22]

[b]N = Number of measurements for mean and relative standard deviation (RSD).

[c]Accuracy is expressed as a percentage of the nominal value for each analyte in the acidified, multi-element solutions.

TABLE 9: MULTILABORATORY ICP PRECISION AND ACCURACY DATA*

Analyte	Concentration µg/L	Total Recoverable Digestion µ/L			
Aluminum	69-4792	X =	0.9380 (C)	+	22.1
		SR =	0.0481 (X)	+	18.8
Antimony	77-1406	X =	0.8908 (C)	+	0.9
		SR =	0.0682 (X)	+	2.5
Arsenic	69-1887	X =	1.0175 (C)	+	3.9
		SR =	0.0643 (X)	+	10.3
Barium	9-377	X =	0.8380 (C)	+	1.68
		SR =	0.0826 (X)	+	3.54
Beryllium	3-1906	X =	1.0177 (C)	-	0.55
		SR =	0.0445 (X)	-	0.10
Boron	19-5189	X =	0.9676 (C)	+	18.7
		SR =	0.0743 (X)	+	21.1
Cadmium	9-1943	X =	1.0137 (C)	-	0.65
		SR =	0.0332 (X)	+	0.90
Calcium	17-47170	X =	0.9658 (C)	+	0.8
		SR =	0.0327 (X)	+	10.1
Chromium	13-1406	X =	1.0049 (C)	-	1.2
		SR =	0.0571 (X)	+	1.0
Cobalt	17-2340	X =	0.9278 (C)	-	1.5
		SR =	0.0407 (X)	+	0.4
Copper	8-1887	X =	0.9647 (C)	-	3.64
		SR =	0.0406 (X)	+	0.96
Iron	13-9359	X =	0.9830 (C)	+	5.7
		SR =	0.0790 (X)	+	11.5
Lead	42-4717	X =	1.0056 (C)	+	4.1
		SR =	0.0448 (X)	+	3.5

* - Regression equations abstracted from Reference 16.
X = Mean Recovery, µg/L.
C = True Value for the Concentration, µg/L.
SR = Single-analyst Standard Deviation, µg/L.

TABLE 9: MULTILABORATORY ICP PRECISION AND ACCURACY DATA*

Analyte	Concentration µg/L	Total Recoverable Digestion µ/L			
Magnesium	34-13868	X =	0.9879 (C)	+	2.2
		SR =	0.0268 (X)	+	8.1
Manganese	4-1887	X =	0.9725 (C)	+	0.07
		SR =	0.0400 (X)	+	0.82
Molybdenum	17-1830	X =	0.9707 (C)	-	2.3
		SR =	0.0529 (X)	+	2.1
Nickel	17-47170	X =	0.9869 (C)	+	1.5
		SR =	0.0393 (X)	+	2.2
Potassium	347-14151	X =	0.9355 (C)	-	183.1
		SR =	0.0329 (X)	+	60.9
Selenium	69-1415	X =	0.9737 (C)	-	1.0
		SR =	0.0443 (X)	+	6.6
Silicon	189-9434	X =	0.9737 (C)	-	60.8
		SR =	0.2133 (X)	+	22.6
Silver	8-189	X =	0.3987 (C)	+	8.25
		SR =	0.1836 (X)	-	0.27
Sodium	35-47170	X =	1.0526 (C)	+	26.7
		SR =	0.0884 (X)	+	50.5
Thallium	79-1434	X =	0.9238 (C)	+	5.5
		SR =	-0.0106 (X)	+	48.0
Vanadium	13-4698	X =	0.9551 (C)	+	0.4
		SR =	0.0472 (X)	+	0.5
Zinc	7-7076	X =	0.9500 (C)	+	1.82
		SR =	0.0153 (X)	+	7.78

* - Regression equations abstracted from Reference 16.
X = Mean Recovery, µg/L.
C = True Value for the Concentration, µg/L.
SR = Single-analyst Standard Deviation, µg/L.

Pb-Cu ICP-AES EMISSION PROFILE

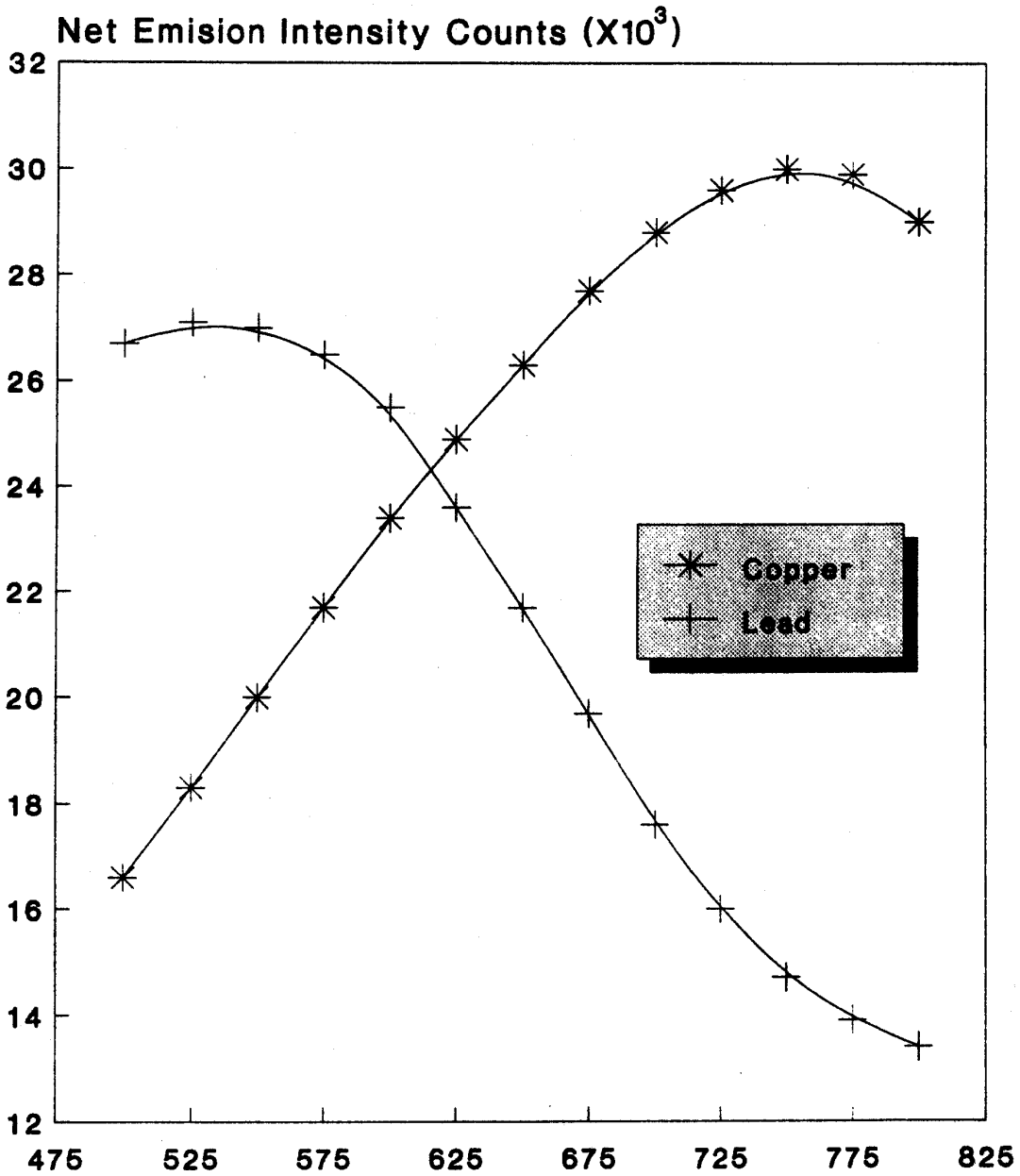

Figure 1

This document does not substitute for EPA regulations; nor is it a regulation itself. Thus, it does not and cannot impose legally binding requirements on the EPA, the states, tribes or the regulated community, and may not apply to a particular situation based on the circumstances. If there are any differences between this web document and the statute or regulations related to this document, the statute and/or regulations govern. The EPA may change this guidance in the future.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

OCT 1 1993

OFFICE OF WATER

MEMORANDUM

SUBJECT: Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Metals Criteria

FROM: Martha G. Prothro
Acting Assistant Administrator for Water

TO: Water Management Division Directors
Environmental Services Division Directors
Regions I-X

Introduction

The implementation of metals criteria is complex due to the site-specific nature of metals toxicity. We have undertaken a number of activities to develop guidance in this area, notably the Interim Metals Guidance, published May 1992, and a public meeting of experts held in Annapolis, MD, in January 1993. This memorandum transmits Office of Water (OW) policy and guidance on the interpretation and implementation of aquatic life criteria for the management of metals and supplements my April 1, 1993, memorandum on the same subject. The issue covers a number of areas including the expression of aquatic life criteria; total maximum daily loads (TMDLs), permits, effluent monitoring, and compliance; and ambient monitoring. The memorandum covers each in turn. Attached to this policy memorandum are three guidance documents with additional technical details. They are: Guidance Document on Expression of Aquatic Life Criteria as Dissolved Criteria (Attachment #2), Guidance Document on Dynamic Modeling and Translators (Attachment #3), and Guidance Document on Monitoring (Attachment #4). These will be supplemented as additional data become available. (See the schedule in Attachment #1.)

Since metals toxicity is significantly affected by site-specific factors, it presents a number of programmatic challenges. Factors that must be considered in the management of metals in the aquatic environment include: toxicity specific to effluent chemistry; toxicity specific to ambient water chemistry; different patterns of toxicity for different metals; evolution of the state of the science of metals toxicity, fate, and transport; resource limitations for monitoring, analysis, implementation, and research functions; concerns regarding some of the analytical data currently on record due to possible sampling and analytical contamination; and lack of standardized protocols for clean and ultraclean metals analysis. The States have the key role in the risk management process of balancing these factors in the management of water programs. The site-specific nature of this issue could be perceived as requiring a permit-by-permit approach to implementation. However, we believe

that this guidance can be effectively implemented on a broader level, across any waters with roughly the same physical and chemical characteristics, and recommend that we work with the States with that perspective in mind.

Expression of Aquatic Life Criteria

o Dissolved vs. Total Recoverable Metal

A major issue is whether, and how, to use dissolved metal concentrations ("dissolved metal") or total recoverable metal concentrations ("total recoverable metal") in setting State water quality standards. In the past, States have used both approaches when applying the same Environmental Protection Agency (EPA) criteria numbers. Some older criteria documents may have facilitated these different approaches to interpretation of the criteria because the documents were somewhat equivocal with regards to analytical methods. The May 1992 interim guidance continued the policy that either approach was acceptable.

It is now the policy of the Office of Water that the use of dissolved metal to set and measure compliance with water quality standards is the recommended approach, because dissolved metal more closely approximates the bioavailable fraction of metal in the water column than does total recoverable metal. This conclusion regarding metals bioavailability is supported by a majority of the scientific community within and outside the Agency. One reason is that a primary mechanism for water column toxicity is adsorption at the gill surface which requires metals to be in the dissolved form.

The position that the dissolved metals approach is more accurate has been questioned because it neglects the possible toxicity of particulate metal. It is true that some studies have indicated that particulate metals appear to contribute to the toxicity of metals, perhaps because of factors such as desorption of metals at the gill surface, but these same studies indicate the toxicity of particulate metal is substantially less than that of dissolved metal.

Furthermore, any error incurred from excluding the contribution of particulate metal will generally be compensated by other factors which make criteria conservative. For example, metals in toxicity tests are added as simple salts to relatively clean water. Due to the likely presence of a significant concentration of metals binding agents in many discharges and ambient waters, metals in toxicity tests would generally be expected to be more bioavailabile than metals in discharges or in ambient waters.

If total recoverable metal is used for the purpose of water quality standards, compounding of factors due to the lower bioavailability of particulate metal and lower bioavailability of metals as they are discharged may result in a conservative water quality standard. The use of dissolved metal in water quality standards gives a more accurate result. However, the majority of the participants at the Annapolis meeting felt that total recoverable measurements in ambient water had some value, and that exceedences of criteria on a total recoverable basis were an indication that metal loadings could be a stress to the ecosystem, particularly in locations other than the water column.

The reasons for the potential consideration of total recoverable measurements include risk management considerations not covered by evaluation of water column toxicity. The ambient water quality criteria are neither designed nor intended to protect sediments, or to prevent effects due to food webs containing sediment dwelling organisms. A risk manager, however, may consider sediments and food chain effects and may decide to take a conservative approach for metals, considering that metals are very persistent chemicals. This conservative approach could include the use of total recoverable metal in water quality standards. However, since consideration of sediment impacts is not incorporated into the criteria methodology, the degree of conservatism inherent in the total recoverable approach is unknown. The uncertainty of metal impacts in sediments stem from the lack of sediment criteria and an imprecise understanding of the fate and transport of metals. EPA will continue to pursue research and other activities to close these knowledge gaps.

Until the scientific uncertainties are better resolved, a range of different risk management decisions can be justified. EPA recommends that State water quality standards be based on dissolved metal. (See the paragraph below and the attached guidance for technical details on developing dissolved criteria.) EPA will also approve a State risk management decision to adopt standards based on total recoverable metal, if those standards are otherwise approvable as a matter of law.

o Dissolved Criteria

In the toxicity tests used to develop EPA metals criteria for aquatic life, some fraction of the metal is dissolved while some fraction is bound to particulate matter. The present criteria were developed using total recoverable metal measurements or measures expected to give equivalent results in toxicity tests, and are articulated as total recoverable. Therefore, in order to express the EPA criteria as dissolved, a total recoverable to dissolved correction factor must be used. Attachment #2 provides guidance for calculating EPA dissolved criteria from the published total recoverable criteria. The data expressed as percentage metal dissolved are presented as recommended values and ranges. However, the choice within ranges is a State risk management decision. We have recently supplemented the data for copper and are proceeding to further supplement the data for copper and other metals. As testing is completed, we will make this information available and this is expected to reduce the magnitude of the ranges for some of the conversion factors provided. We also strongly encourage the application of dissolved criteria across a watershed or waterbody, as technically sound and the best use of resources.

o Site-Specific Criteria Modifications

While the above methods will correct some site-specific factors affecting metals toxicity, further refinements are possible. EPA has issued guidance (Water Quality Standards Handbook, 1983; Guidelines for Deriving Numerical Aquatic Site-Specific Water Quality Criteria by Modifying National Criteria, EPA-600/3-H4-099, October 1984) for three site-specific criteria development methodologies: recalculation procedure, indicator species procedure (also known as the water-effect ratio (WER)) and resident species procedure. Only the first two of these have been widely used.

In the National Toxics Rule (57 FR 60848, December 22, 1992), EPA identified the WER as an optional method for site-specific criteria development for certain metals. EPA committed in the NTR preamble to provide guidance on determining the WER. A draft of this guidance has been circulated to the States and Regions for review and comment. As justified by water characteristics and as recommended by the WER guidance, we strongly encourage the application of the WER across a watershed or waterbody as opposed to application on a discharger by discharger basis, as technically sound and an efficient use of resources.

In order to meet current needs, but allow for changes suggested by protocol users, EPA will issue the guidance as "interim." EPA will accept WERs developed using this guidance, as well as by using other scientifically defensible protocols. OW expects the interim WER guidance will be issued in the next two months.

Total Maximum Daily Loads (TMDLs) and National Pollutant Discharge Elimination System (NPDES) Permits

o Dynamic Water Quality Modeling

Although not specifically part of the reassessment of water quality criteria for metals, dynamic or probabilistic models are another useful tool for implementing water quality criteria, especially for those criteria protecting aquatic life. These models provide another way to incorporate site-specific data. The 1991 Technical Support Document for Water Quality-based Toxics Control (TSD) (EPA/505/2-90-001) describes dynamic, as well as static (steady-state) models. Dynamic models make the best use of the specified magnitude, duration, and frequency of water quality criteria and, therefore, provide a more accurate representation of the probability that a water quality standard exceedence will occur. In contrast, steady-state models make a number of simplifying, worst case assumptions which makes them less complex and less accurate than dynamic models.

Dynamic models have received increased attention over the last few years as a result of the widespread belief that steady-state modeling is over-conservative due to environmentally conservative dilution assumptions. This belief has led to the misconception that dynamic models will always lead to less stringent regulatory controls (e.g., NPDES effluent limits) than steady-state models, which is not true in every application of dynamic models. EPA considers dynamic models to be a more accurate approach to implementing water quality criteria and continues to recommend their use. Dynamic modeling does require commitment of resources to develop appropriate data. (See Attachment #3 and the TSD for details on the use of dynamic models.)

o Dissolved-Total Metal Translators

Expressing water quality criteria as the dissolved form of a metal poses a need to be able to translate from dissolved metal to total recoverable metal for TMDLs and NPDES permits. TMDLs for metals must be able to calculate: (1) dissolved metal in order to ascertain attainment of water quality standards, and (2) total recoverable metal in order to achieve mass balance necessary for permitting purposes.

EPA's NPDES regulations require that limits of metals in permits be stated as total recoverable in most cases (see 40 CFR §122.45(c)) except when an effluent guideline specifies the limitation in another form of the metal, the approved analytical methods measure only dissolved metal, or the permit writer expresses a metals limit in another form (e.g., dissolved, valent, or total) when required to carry out provisions of the Clean Water Act. This is because the chemical conditions in ambient waters frequently differ substantially from those in the effluent; and there is no assurance that effluent particulate metal would not dissolve after discharge. The NPDES rule does not require that State water quality standards be expressed as total recoverable; rather, the rule requires permit writers to translate between different metal forms in the calculation of the permit limit so that a total recoverable limit can be established. Both the TMDL and NPDES uses of water quality criteria require the ability to translate between dissolved metal and total recoverable metal. Attachment #3 provides methods for this translation.

Guidance on Monitoring

o Use of Clean Sampling and Analytical Techniques

In assessing waterbodies to determine the potential for toxicity problems due to metals, the quality of the data used is an important issue. Metals data are used to determine attainment status for water quality standards, discern trends in water quality, estimate background loads for TMDLs, calibrate fate and transport models, estimate effluent concentrations (including effluent variability), assess permit compliance, and conduct research. The quality of trace level metal data, especially below 1 ppb, may be compromised due to contamination of samples during collection, preparation, storage, and analysis. Depending on the level of metal present, the use of "clean" and "ultraclean" techniques for sampling and analysis may be critical to accurate data for implementation of aquatic life criteria for metals.

The magnitude of the contamination problem increases as the ambient and effluent metal concentration decreases and, therefore, problems are more likely in ambient measurements. "Clean" techniques refer to those requirements (or practices for sample collection and handling) necessary to produce reliable analytical data in the part per billion (ppb) range. "Ultraclean" techniques refer to those requirements or practices necessary to produce reliable analytical data in the part per trillion (ppt) range. Because typical concentrations of metals in surface waters and effluents vary from one metal to another, the effect of contamination on the quality of metals monitoring data varies appreciably.

We plan to develop protocols on the use of clean and ultra-clean techniques and are coordinating with the United States Geological Survey (USGS) on this project, because USGS has been doing work on these techniques for some time, especially the sampling procedures. We anticipate that our draft protocols for clean techniques will be available in late calendar year 1993. The development of comparable protocols for ultra-clean techniques is underway and will be available in 1995. In developing these protocols, we will consider the costs of these techniques and will give guidance as to the situations where their use is necessary. Appendix B to the WER guidance document provides some general guidance on the use of

clean analytical techniques. (See Attachment #4.) We recommend that this guidance be used by States and Regions as an interim step, while the clean and ultra-clean protocols are being developed.

o Use of Historical Data

The concerns about metals sampling and analysis discussed above raise corresponding concerns about the validity of historical data. Data on effluent and ambient metal concentrations are collected by a variety of organizations including Federal agencies (e.g., EPA, USGS), State pollution control agencies and health departments, local government agencies, municipalities, industrial dischargers, researchers, and others. The data are collected for a variety of purposes as discussed above.

Concern about the reliability of the sample collection and analysis procedures is greatest where they have been used to monitor very low level metal concentrations. Specifically, studies have shown data sets with contamination problems during sample collection and laboratory analysis, that have resulted in inaccurate measurements. For example, in developing a TMDL for New York Harbor, some historical ambient data showed extensive metals problems in the harbor, while other historical ambient data showed only limited metals problems. Careful resampling and analysis in 1992/1993 showed the latter view was correct. The key to producing accurate data is appropriate quality assurance (QA) and quality control (QC) procedures. We believe that most historical data for metals, collected and analyzed with appropriate QA and QC at levels of 1 ppb or higher, are reliable. The data used in development of EPA criteria are also considered reliable, both because they meet the above test and because the toxicity test solutions are created by adding known amounts of metals.

With respect to effluent monitoring reported by an NPDES permittee, the permittee is responsible for collecting and reporting quality data on a Discharge Monitoring Report (DMR). Permitting authorities should continue to consider the information reported to be true, accurate, and complete as certified by the permittee. Where the permittee becomes aware of new information specific to the effluent discharge that questions the quality of previously submitted DMR data, the permittee must promptly submit that information to the permitting authority. The permitting authority will consider all information submitted by the permittee in determining appropriate enforcement responses to monitoring/reporting and effluent violations. (See Attachment #4 for additional details.)

Summary

The management of metals in the aquatic environment is complex. The science supporting our technical and regulatory programs is continuing to evolve, here as in all areas. The policy and guidance outlined above represent the position of OW and should be incorporated into ongoing program operations. We do not expect that ongoing operations would be delayed or deferred because of this guidance.

If you have questions concerning this guidance, please contact Jim Hanlon, Acting Director, Office of Science and Technology, at 202-260-5400. If you have questions on specific details of the guidance, please contact the appropriate OW Branch Chief. The Branch Chiefs responsible for the various areas of the water quality program are: Bob April (202-260-6322, water quality criteria), Elizabeth Fellows (202-260-7046, monitoring and data issues), Russ Kinerson (202-260-1330, modeling and translators), Don Brady (202-260-7074, Total Maximum Daily Loads), Sheila Frace (202-260-9537, permits), Dave Sabock (202-260-1315, water quality standards), Bill Telliard (202-260-7134, analytical methods) and Dave Lyons (202-260-8310, enforcement).

Attachments

ATTACHMENT #1

TECHNICAL GUIDANCE FOR METALS

Schedule of Upcoming Guidance

Water-effect Ratio Guidance - September 1993

Draft "Clean" Analytical Methods - Spring 1994

Dissolved Criteria - currently being done; as testing is completed, we will release the updated percent dissolved data

Draft Sediment Criteria for Metals - 1994

Final Sediment Criteria for Metals - 1995

ATTACHMENT #2

GUIDANCE DOCUMENT
ON DISSOLVED CRITERIA
Expression of Aquatic Life Criteria
October 1993

NMMA Exhibit 5

Percent Dissolved in Aquatic Toxicity Tests on Metals

The attached table contains all the data that were found concerning the percent of the total recoverable metal that was dissolved in aquatic toxicity tests. This table is intended to contain the available data that are relevant to the conversion of EPA's aquatic life criteria for metals from a total recoverable basis to a dissolved basis. (A factor of 1.0 is used to convert aquatic life criteria for metals that are expressed on the basis of the acid-soluble measurement to criteria expressed on the basis of the total recoverable measurement.) Reports by Grunwald (1992) and Brungs et al. (1992) provided references to many of the documents in which pertinent data were found. Each document was obtained and examined to determine whether it contained useful data.

"Dissolved" is defined as metal that passes through a 0.45-µm membrane filter. If otherwise acceptable, data that were obtained using 0.3-µm glass fiber filters and 0.1-µm membrane filters were used, and are identified in the table; these data did not seem to be outliers.

Data were used only if the metal was in a dissolved inorganic form when it was added to the dilution water. In addition, data were used only if they were generated in water that would have been acceptable for use as a dilution water in tests used in the derivation of water quality criteria for aquatic life; in particular, the pH had to be between 6.5 and 9.0, and the concentrations of total organic carbon (TOC) and total suspended solids (TSS) had to be below 5 mg/L. Thus most data generated using river water would not be used.

Some data were not used for other reasons. Data presented by Carroll et al. (1979) for cadmium were not used because 9 of the 36 values were above 150%. Data presented by Davies et al. (1976) for lead and Holcombe and Andrew (1978) for zinc were not used because "dissolved" was defined on the basis of polarography, rather than filtration.

Beyond this, the data were not reviewed for quality. Horowitz et al. (1992) reported that a number of aspects of the filtration procedure might affect the results. In addition, there might be concern about use of "clean techniques" and adequate QA/QC.

Each line in the table is intended to represent a separate piece of information. All of the data in the table were determined in fresh water, because no saltwater data were found. Data are becoming available for copper in salt water from the New York

Harbor study; based on the first set of tests, Hansen (1993) suggested that the average percent of the copper that is dissolved in sensitive saltwater tests is in the range of 76 to 82 percent.

A thorough investigation of the percent of total recoverable metal that is dissolved in toxicity tests might attempt to determine if the percentage is affected by test technique (static, renewal, flow-through), feeding (were the test animals fed and, if so, what food and how much), water quality characteristics (hardness, alkalinity, pH, salinity), test organisms (species, loading), etc.

The attached table also gives the freshwater criteria concentrations (CMC and CCC) because percentages for total recoverable concentrations much (e.g., more than a factor of 3) above or below the CMC and CCC are likely to be less relevant. When a criterion is expressed as a hardness equation, the range given extends from a hardness of 50 mg/L to a hardness of 200 mg/L.

The following is a summary of the available information for each metal:

Arsenic(III)

The data available indicate that the percent dissolved is about 100, but all the available data are for concentrations that are much higher than the CMC and CCC.

Cadmium

Schuytema et al. (1984) reported that "there were no real differences" between measurements of total and dissolved cadmium at concentrations of 10 to 80 ug/L (pH = 6.7 to 7.8, hardness = 25 mg/L, and alkalinity = 33 mg/L); total and dissolved concentrations were said to be "virtually equivalent".

The CMC and CCC are close together and only range from 0.66 to 8.6 ug/L. The only available data that are known to be in the range of the CMC and CCC were determined with a glass fiber filter. The percentages that are probably most relevant are 75, 92, 89, 78, and 80.

Chromium(III)

The percent dissolved decreased as the total recoverable concentration increased, even though the highest concentrations reduced the pH substantially. The percentages that are probably

most relevant to the CMC are 50-75, whereas the percentages that are probably most relevant to the CCC are 86 and 61.

Chromium(VI)

The data available indicate that the percent dissolved is about 100, but all the available data are for concentrations that are much higher than the CMC and CCC.

Copper

Howarth and Sprague (1978) reported that the total and dissolved concentrations of copper were "little different" except when the total copper concentration was above 500 ug/L at hardness = 360 mg/L and pH = 8 or 9. Chakoumakos et al. (1979) found that the percent dissolved depended more on alkalinity than on hardness, pH, or the total recoverable concentration of copper.

Chapman (1993) and Lazorchak (1987) both found that the addition of daphnid food affected the percent dissolved very little, even though Chapman used yeast-trout chow-alfalfa whereas Lazorchak used algae in most tests, but yeast-trout chow-alfalfa in some tests. Chapman (1993) found a low percent dissolved with and without food, whereas Lazorchak (1987) found a high percent dissolved with and without food. All of Lazorchak's values were in high hardness water; Chapman's one value in high hardness water was much higher than his other values.

Chapman (1993) and Lazorchak (1987) both compared the effect of food on the total recoverable LC50 with the effect of food on the dissolved LC50. Both authors found that food raised both the dissolved LC50 and the total recoverable LC50 in about the same proportion, indicating that food did not raise the total recoverable LC50 by sorbing metal onto food particles; possibly the food raised both LC50s by (a) decreasing the toxicity of dissolved metal, (b) forming nontoxic dissolved complexes with the metal, or (c) reducing uptake.

The CMC and CCC are close together and only range from 6.5 to 34 ug/L. The percentages that are probably most relevant are 74, 95, 95, 73, 57, 53, 52, 64, and 91.

Lead

The data presented in Spehar et al. (1978) were from Holcombe et al. (1976). Both Chapman (1993) and Holcombe et al. (1976) found that the percent dissolved increased as the total recoverable concentration increased. It would seem reasonable to expect more precipitate at higher total recoverable concentrations and

therefore a lower percent dissolved at higher concentrations. The increase in percent dissolved with increasing concentration might be due to a lowering of the pH as more metal is added if the stock solution was acidic.

The percentages that are probably most relevant to the CMC are 9, 18, 25, 10, 62, 68, 71, 75, 81, and 95, whereas the percentages that are probably most relevant to the CCC are 9 and 10.

Mercury

The only percentage that is available is 73, but it is for a concentration that is much higher than the CMC.

Nickel

The percentages that are probably most relevant to the CMC are 88, 93, 92, and 100, whereas the only percentage that is probably relevant to the CCC is 76.

Selenium

No data are available.

Silver

There is a CMC, but not a CCC. The percentage dissolved seems to be greatly reduced by the food used to feed daphnids, but not by the food used to feed fathead minnows. The percentages that are probably most relevant to the CMC are 41, 79, 79, 73, 91, 90, and 93.

Zinc

The CMC and CCC are close together and only range from 59 to 210 ug/L. The percentages that are probably most relevant are 31, 77, 77, 99, 94, 100, 103, and 96.

Recommended Values (%)[A] and Ranges of Measured Percent Dissolved Considered Most Relevant in Fresh Water

Metal	CMC		CCC	
	Recommended Value (%)	(Range %)	Recommended Value (%)	(Range %)
Arsenic(III)	95	100-104[B]	95	100-104[B]
Cadmium	85	75-92	85	75-92
Chromium(III)	85	50-75	85	61-86
Chromium(VI)	95	100[B]	95	100[B]
Copper	85	52-95	85	52-95
Lead	50	9-95	25	9-10
Mercury	85	73[B]	NA[E]	NA[E]
Nickel	85	88-100	85	76
Selenium	NA[E]	NA[C]	NA[E]	NA[C]
Silver	85	41-93	YY[D]	YY[D]
Zinc	85	31-103	85	31-103

[A] The recommended values are based on current knowledge and are subject to change as more data becomes available.

[B] All available data are for concentrations that are much higher than the CMC.

[C] NA = No data are available.

[D] YY = A CCC is not available, and therefore cannot be adjusted.

[E] NA = Bioaccumulative chemical and not appropriate to adjust to percent dissolved.

Concn.[A] (ug/L)	Percent Diss.[B]	n[C]	Species[D]	SRF[E]	Food	Hard.	Alk.	pH	Ref.
ARSENIC(III) (Freshwater: CCC = 190 ug/L; CMC = 360 ug/L)									
600-15000	104	5	?	?	?	48	41	7.6	Lima et al. 1984
12600	100	3	FM	F	No	44	43	7.4	Spehar and Fiandt 1986
CADMIUM (Freshwater: CCC = 0.66 to 2.0 ug/L; CMC = 1.8 to 8.6 ug/L)[F]									
0.16	41	?	DM	R	Yes	53	46	7.6	Chapman 1993
0.28	75	?	DM	R	Yes	103	83	7.9	Chapman 1993
0.4-4.0	92[G]	?	CS	F	No	21	19	7.1	Finlayson and Verrue 1982
13	89	3	FM	F	No	44	43	7.4	Spehar and Fiandt 1986
15-21	96	8	FM	S	No	42	31	7.5	Spehar and Carlson 1984
42	84	4	FM	S	No	45	41	7.4	Spehar and Carlson 1984
10	78	?	DM	S	No	51	38	7.5	Chapman 1993
35	77	?	DM	S	No	105	88	8.0	Chapman 1993
51	59	?	DM	S	No	209	167	8.4	Chapman 1993
6-80	80	8	?	S	No	47	44	7.5	Call et al. 1982
3-232	90[H]	5	?	F	?	46	42	7.4	Spehar et al. 1978
450-6400	70	5	FM	F	No	202	157	7.7	Pickering and Gast 1972

CHROMIUM(III) (Freshwater: CCC = 120 to 370 ug/L; CMC = 980 to 3100 ug/L)[F]

5-13	94	?	SG	F	?	25	24	7.3	Stevens and Chapman 1984
19-495	86	?	SG	F	?	25	24	7.2	Stevens and Chapman 1984
>1100	50-75	?	SG	F	No	25	24	7.0	Stevens and Chapman 1984
42	54	?	DM	R	Yes	206	166	8.2	Chapman 1993
114	61	?	DM	R	Yes	52	45	7.4	Chapman 1993
16840	26	?	DM	S	No	<51	9	6.3[I]	Chapman 1993
26267	32	?	DM	S	No	110	9	6.7	Chapman 1993
27416	27	?	DM	S	No	96	10	6.0[I]	Chapman 1993
58665	23	?	DM	S	No	190	25	6.2[I]	Chapman 1993

CHROMIUM(VI) (Freshwater: CCC = 11 ug/L; CMC = 16 ug/L)

>25,000	100	1	FM,GF	F	Yes	220	214	7.6	Adelman and Smith 1976
43,300	99.5	4	FM	F	No	44	43	7.4	Spehar and Fiandt 1986

COPPER (Freshwater: CCC = 6.5 to 21 ug/L; CMC = 9.2 to 34 ug/L)[F]

10-30	74	?	CT	F	No	27	20	7.0	Chakoumakos et al. 1979
40-200	78	?	CT	F	No	154	20	6.8	Chakoumakos et al. 1979
30-100	79	?	CT	F	No	74	23	7.6	Chakoumakos et al. 1979
100-200	82	?	CT	F	No	192	72	7.0	Chakoumakos et al. 1979
20-200	86	?	CT	F	No	31	78	8.3	Chakoumakos et al. 1979
40-300	87	?	CT	F	No	83	70	7.4	Chakoumakos et al. 1979
10-80	89	?	CT	F	No	25	169	8.5	Chakoumakos et al. 1979

300-1300	92	?	CT	F	No	195	160	7.0	Chakoumakos et al. 1979
100-400	94	?	CT	F	No	70	174	8.5	Chakoumakos et al. 1979
3-4[J]	125-167	2	CD	R	Yes	31	38	7.2	Carlson et al. 1986a,b
12-91[J]	79-84	3	CD	R	Yes	31	38	7.2	Carlson et al. 1986a,b
18-19	95	2	DA	S	No	52	55	7.7	Carlson et al. 1986b
20[J]	95	1	DA	R	No	31	38	7.2	Carlson et al. 1986b
50	96	2	FM	S	No	52	55	7.7	Carlson et al. 1986b
175[J]	91	2	FM	R	No	31	38	7.2	Carlson et al. 1986b
5-52	>82[K]	?	FM	F	Yes[L]	47	43	8.0	Lind et al. 1978
6-80	83[Q]	?	CS	F	No	21	19	7.1	Finlayson and Verrue 1982
6.7	57	?	DM	S	No	49	37	7.7	Chapman 1993
35	43	?	DM	S	Yes	48	39	7.4	Chapman 1993
13	73	?	DM	R	Yes	211	169	8.1	Chapman 1993
16	57	?	DM	R	Yes	51	44	7.6	Chapman 1993
51	39	?	DM	R	Yes	104	83	7.8	Chapman 1993
32	53	?	DM	S	No	52	45	7.8	Chapman 1993
33	52	?	DM	S	No	105	79	7.9	Chapman 1993
39	64	?	DM	S	No	106	82	8.1	Chapman 1993
25-84	96	14	FM,GM	S	No	50	40	7.0	Hammermeister et al. 1983
17	91	6	DM	S	No	52	43	7.3	Hammermeister et al. 1983
120	88	14	SG	S	No	48	47	7.3	Hammermeister et al. 1983
15-90	74	19	?	S	No	48	47	7.7	Call et al. 1982
12-162	80[M]	?	BG	F	Yes[L]	45	43	7-8	Benoit 1975
28-58	85	6	DM	R	No	168	117	8.0	Lazorchak 1987
26-59	79	7	DM	R	Yes[M]	168	117	8.0	Lazorchak 1987
56,101	86	2	DM	R	Yes[N]	168	117	8.0	Lazorchak 1987

96	86	4	FM	F	No	44	43	7.4	Spehar and Fiandt 1986
160	94	1	FM	S	No	203	171	8.2	Geckler et al. 1976
230-3000	>69->79	?	CR	F	No	17	13	7.6	Rice and Harrison 1983
LEAD (Freshwater: CCC = 1.3 to 7.7 ug/L; CMC = 34 to 200 ug/L)[F]									
17	9	?	DM	R	Yes	52	47	7.6	Chapman 1993
181	18	?	DM	R	Yes	102	86	7.8	Chapman 1993
193	25	?	DM	R	Yes	151	126	8.1	Chapman 1993
612	29	?	DM	S	No	50	--	---	Chapman 1993
952	33	?	DM	S	No	100	--	---	Chapman 1993
1907	-38	?	DM	S	No	150	--	---	Chapman 1993
7-29	10	?	EZ	R	No	22	--	---	JRB Associates 1983
34	62[M]	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
58	68[M]	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
119	71[M]	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
235	75[M]	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
474	81[M]	?	BT	F	Yes	44	43	7.2	Holcombe et al. 1976
4100	82[M]	?	BT	F	No	44	43	7.2	Holcombe et al. 1976
2100	79	7	FM	F	No	44	43	7.4	Spehar and Fiandt 1986
220-2700	96	14	FM,GM,DM	S	No	49	44	7.2	Hammermeister et al. 1983
580	95	14	SG	S	No	51	48	7.2	Hammermeister et al. 1983
MERCURY(II) (Freshwater: CMC = 2.4 ug/L)									
172	73	1	FM	F	No	44	43	7.4	Spehar and Fiandt 1986

NICKEL (Freshwater: CCC = 88 to 280 ug/L; CMC = 790 to 2500 ug/L)[F]

21	81	?	DM	R	Yes	51	49	7.4	Chapman 1993
150	76	?	DM	R	Yes	107	87	7.8	Chapman 1993
578	87	?	DM	R	Yes	205	161	8.1	Chapman 1993
645	88	?	DM	S	No	54	43	7.7	Chapman 1993
1809	93	?	DM	S	No	51	44	7.7	Chapman 1993
1940	92	?	DM	S	No	104	84	8.2	Chapman 1993
2344	100	?	DM	S	No	100	84	7.9	Chapman 1993
4000	90	?	PK	R	No	21	--	---	JRB Associates 1983

SELENIUM (FRESHWATER: CCC = 5 ug/L; CMC = 20 ug/L)

No data are available.

SILVER (Freshwater: CMC = 1.2 to 13 ug/L; a CCC is not available)

0.19	74	?	DM	S	No	47	37	7.6	Chapman 1993
9.98	13	?	DM	S	Yes	47	37	7.5	Chapman 1993
4.0	41	?	DM	S	No	36	25	7.0	Nebeker et al. 1983
4.0	11	?	DM	S	Yes	36	25	7.0	Nebeker et al. 1983
3	79	?	FM	S	No	51	49	8.1	UWS 1993
2-54	79	?	FM	S	Yes[O]	49	49	7.9	UWS 1993
2-32	73	?	FM	S	No	50	49	8.1	UWS 1993
4-32	91	?	FM	S	No	48	49	8.1	UWS 1993
5-89	90	?	FM	S	No	120	49	8.2	UWS 1993
6-401	93	?	FM	S	No	249	49	8.1	UWS 1993

ZINC (Freshwater: CCC = 59 to 190 ug/L; CMC 65 to 210 ug/L)[F]

52	31	?	DM	R	Yes	211	169	8.2	Chapman 1993
62	77	?	DM	R	Yes	104	83	7.8	Chapman 1993
191	77	?	DM	R	Yes	52	47	7.5	Chapman 1993
356	74	?	DM	S	No	54	47	7.6	Chapman 1993
551	78	?	DM	S	No	105	85	8.1	Chapman 1993
741	76	?	DM	S	No	196	153	8.2	Chapman 1993
7[I]	71-129	2	CD	R	Yes	31	38	7.2	Carlson et al. 1986b
18-273[I]	81-107	2	CD	R	Yes	31	38	7.2	Carlson et al. 1986b
167[I]	99	2	CD	R	No	31	38	7.2	Carlson et al. 1986b
180	94	1	CD	S	No	52	55	7.7	Carlson et al. 1986b
188-393[I]	100	2	FM	R	No	31	38	7.2	Carlson et al. 1986b
551	100	1	FM	S	No	52	55	7.7	Carlson et al. 1986b
40-500	95[O]	?	CS	F	No	21	19	7.1	Finlayson and Verrue 1982
1940	100	?	AS	F	No	20	12	7.1	Sprague 1964
5520	83	?	AS	F	No	20	12	7.9	Sprague 1964
<4000	90	?	FM	F	No	204	162	7.7	Mount 1966
>4000	70	?	FM	F	No	204	162	7.7	Mount 1966
160-400	103	13	FM,GM,DM	S	No	52	43	7.5	Hammermeister et al. 1983
240	96	13	SG	S	No	49	46	7.2	Hammermeister et al. 1983

[A] Total recoverable concentration.

[B] Except as noted, a 0.45-μm membrane filter was used.

[C] Number of paired comparisons.

[D] The abbreviations used are:

AS = Atlantic salmon	DM = Daphnia magna
BT = Brook trout	EZ = Elassoma zonatum
CD = Ceriodaphnia dubia	FM = Fathead minnow
CR = Crayfish	GF = Goldfish
CS = Chinook salmon	GM = Gammarid
CT = Cutthroat trout	PK = Palaemonetes kadiakensis
DA = Daphnids	SG = Salmo gairdneri

[E] The abbreviations used are:

S = static
R = renewal
F = flow-through

[F] The two numbers are for hardnesses of 50 and 200 mg/L, respectively.

[G] A 0.3-μm glass fiber filter was used.

[H] A 0.10-μm membrane filter was used.

[I] The pH was below 6.5.

[J] The dilution water was a clean river water with TSS and TOC below 5 mg/L.

[K] Only limited information is available concerning this value.

[L] It is assumed that the solution that was filtered was from the test chambers that contained fish and food.

[M] The food was algae.

[N] The food was yeast-trout chow-alfalfa.

[O] The food was frozen adult brine shrimp.

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ATTACHMENT #3

GUIDANCE DOCUMENT
ON DYNAMIC MODELING AND TRANSLATORS
August 1993

Total Maximum Daily Loads (TMDLs) and Permits

o Dynamic Water Quality Modeling

Although not specifically part of the reassessment of water quality criteria for metals, dynamic or probabilistic models are another useful tool for implementing water quality criteria, especially those for protecting aquatic life. Dynamic models make best use of the specified magnitude, duration, and frequency of water quality criteria and thereby provide a more accurate calculation of discharge impacts on ambient water quality. In contrast, steady-state modeling is based on various simplifying assumptions which makes it less complex and less accurate than dynamic modeling. Building on accepted practices in water resource engineering, ten years ago OW devised methods allowing the use of probability distributions in place of worst-case conditions. The description of these models and their advantages and disadvantages is found in the 1991 Technical Support Document for Water Quality-based Toxic Control (TSD).

Dynamic models have received increased attention in the last few years as a result of the perception that static modeling is over-conservative due to environmentally conservative dilution assumptions. This has led to the misconception that dynamic models will always justify less stringent regulatory controls (e.g. NPDES effluent limits) than static models. In effluent dominated waters where the upstream concentrations are relatively constant, however, a dynamic model will calculate a more stringent wasteload allocation than will a steady state model. The reason is that the critical low flow required by many State water quality standards in effluent dominated streams occurs more frequently than once every three years. When other environmental factors (e.g. upstream pollutant concentrations) do not vary appreciably, then the overall return frequency of the steady state model may be greater than once in three years. A dynamic modeling approach, on the other hand, would be more stringent, allowing only a once in three year return frequency. As a result, EPA considers dynamic models to be a more accurate rather than a less stringent approach to implementing water quality criteria.

The 1991 TSD provides recommendations on the use of steady state and dynamic water quality models. The reliability of any modeling technique greatly depends on the accuracy of the data used in the analysis. Therefore, the selection of a model also depends upon the data. EPA recommends that steady state wasteload allocation analyses generally be used where few or no whole effluent toxicity or specific chemical measurements are available, or where daily receiving water flow records are not available. Also, if staff resources are insufficient to use and defend the use of dynamic models, then steady state

models may be necessary. If adequate receiving water flow and effluent concentration data are available to estimate frequency distributions, EPA recommends that one of the dynamic wasteload allocation modeling techniques be used to derive wasteload allocations which will more exactly maintain water quality standards. The minimum data required for input into dynamic models include at least 30 years of river flow data and one year of effluent and ambient pollutant concentrations.

o Dissolved-Total Metal Translators

When water quality criteria are expressed as the dissolved form of a metal, there is a need to translate TMDLs and NPDES permits to and from the dissolved form of a metal to the total recoverable form. TMDLs for toxic metals must be able to calculate 1) the dissolved metal concentration in order to ascertain attainment of water quality standards and 2) the total recoverable metal concentration in order to achieve mass balance. In meeting these requirements, TMDLs consider metals to be conservative pollutants and quantified as total recoverable to preserve conservation of mass. The TMDL calculates the dissolved or ionic species of the metals based on factors such as total suspended solids (TSS) and ambient pH. (These assumptions ignore the complicating factors of metals interactions with other metals.) In addition, this approach assumes that ambient factors influencing metal partitioning remain constant with distance down the river. This assumption probably is valid under the low flow conditions typically used as design flows for permitting of metals (e.g., 7Q10, 4B3, etc) because erosion, resuspension, and wet weather loadings are unlikely to be significant and river chemistry is generally stable. In steady-state dilution modeling, metals releases may be assumed to remain fairly constant (concentrations exhibit low variability) with time.

EPA's NPDES regulations require that metals limits in permits be stated as total recoverable in most cases (see 40 CFR §122.45(c)). Exceptions occur when an effluent guideline specifies the limitation in another form of the metal or the approved analytical methods measure only the dissolved form. Also, the permit writer may express a metals limit in another form (e.g., dissolved, valent, or total) when required, in highly unusual cases, to carry out the provisions of the CWA.

The preamble to the September 1984 National Pollutant Discharge Elimination System Permit Regulations states that the total recoverable method measures dissolved metals plus that portion of solid metals that can easily dissolve under ambient conditions (see 49 Federal Register 38028, September 26, 1984). This method is intended to measure metals in the effluent that are or may easily become environmentally active, while not measuring metals that are expected to settle out and remain inert.

The preamble cites, as an example, effluent from an electroplating facility that adds lime and uses clarifiers. This effluent will be a combination of solids not removed by the clarifiers and residual dissolved metals. When the effluent from the clarifiers, usually with a

high pH level, mixes with receiving water having significantly lower pH level, these solids instantly dissolve. Measuring dissolved metals in the effluent, in this case, would underestimate the impact on the receiving water. Measuring with the total metals method, on the other hand, would measure metals that would be expected to disperse or settle out and remain inert or be covered over. Thus, measuring total recoverable metals in the effluent best approximates the amount of metal likely to produce water quality impacts.

However, the NPDES rule does not require in any way that State water quality standards be in the total recoverable form; rather, the rule requires permit writers to consider the translation between differing metal forms in the calculation of the permit limit so that a total recoverable limit can be established. Therefore, both the TMDL and NPDES uses of water quality criteria require the ability to translate from the dissolved form and the total recoverable form.

Many toxic substances, including metals, have a tendency to leave the dissolved phase and attach to suspended solids. The partitioning of toxics between solid and dissolved phases can be determined as a function of a pollutant-specific partition coefficient and the concentration of solids. This function is expressed by a linear partitioning equation:

$$C = \frac{C_{TT}}{1 + K_d \cdot TSS \cdot 10^{-6}}$$

where,

C = dissolved phase metal concentration,
C_{TT} = total metal concentration,
TSS = total suspended solids concentration, and
K_d = partition coefficient.

A key assumption of the linear partitioning equation is that the sorption reaction reaches dynamic equilibrium at the point of application of the criteria; that is, after allowing for initial mixing the partitioning of the pollutant between the adsorbed and dissolved forms can be used at any location to predict the fraction of pollutant in each respective phase.

Successful application of the linear partitioning equation relies on the selection of the partition coefficient. The use of a partition coefficient to represent the degree to which toxics adsorb to solids is most readily applied to organic pollutants; partition coefficients for metals are more difficult to define. Metals typically exhibit more complex speciation and complexation reactions than organics and the degree of partitioning can vary greatly depending upon site-specific water chemistry. Estimated partition coefficients can be determined for a number of metals, but waterbody or site-specific observations of dissolved and adsorbed concentrations are preferred.

EPA suggests three approaches for instances where a water quality criterion for a metal is expressed in the dissolved form in a State's water quality standards:

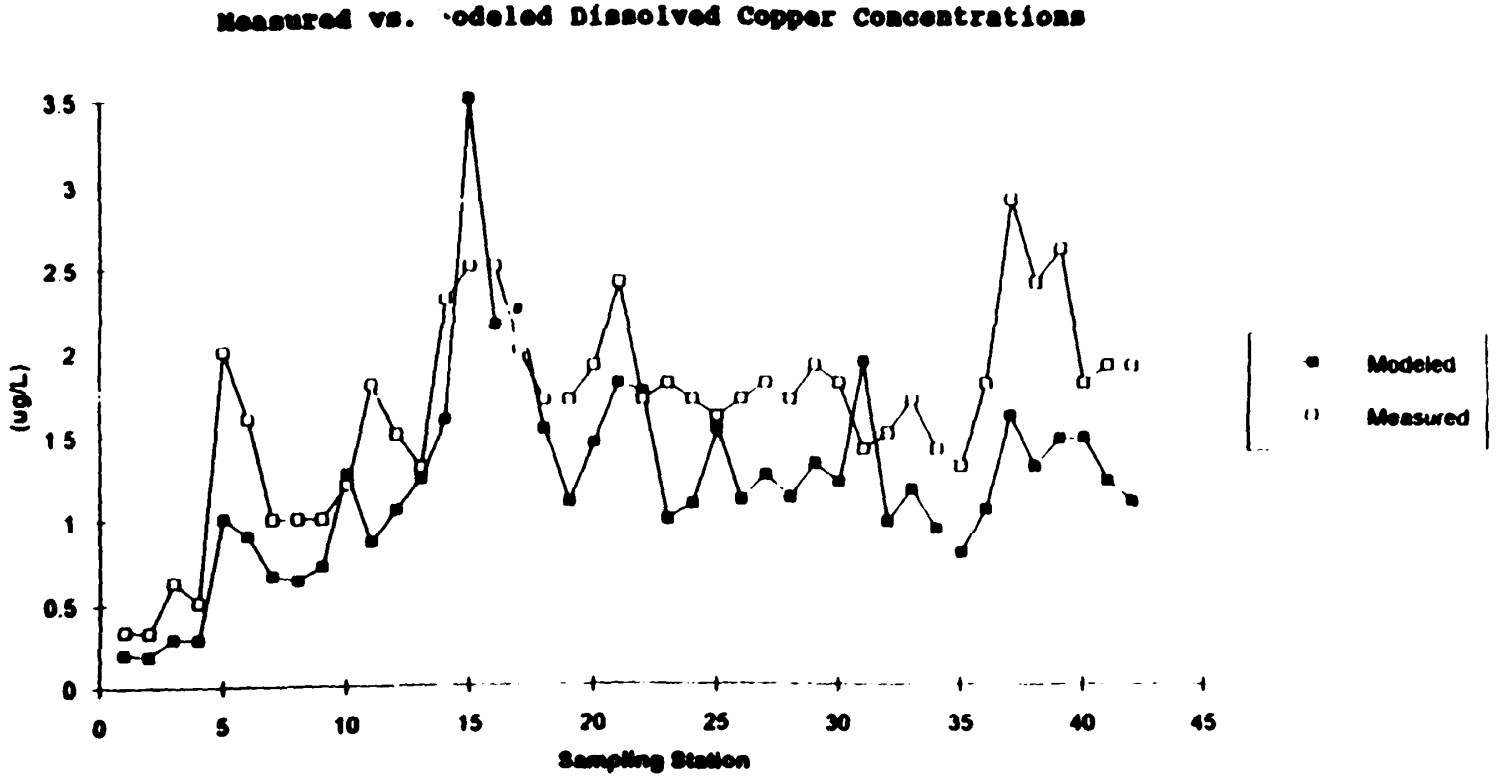
1. Using clean analytical techniques and field sampling procedures with appropriate QA/QC, collect receiving water samples and determine site specific values of K_d for each metal. Use these K_d values to "translate" between total recoverable and dissolved metals in receiving water. This approach is more difficult to apply because it relies upon the availability of good quality measurements of ambient metal concentrations. This approach provides an accurate assessment of the dissolved metal fraction providing sufficient samples are collected. EPA's initial recommendation is that at least four pairs of total recoverable and dissolved ambient metal measurements be made during low flow conditions or 20 pairs over all flow conditions. EPA suggests that the average of data collected during low flow or the 95th percentile highest dissolved fraction for all flows be used. The low flow average provides a representative picture of conditions during the rare low flow events. The 95th percentile highest dissolved fraction for all flows provides a critical condition approach analogous to the approach used to identify low flows and other critical environmental conditions.

2. Calculate the total recoverable concentration for the purpose of setting the permit limit. Use a value of 1 unless the permittee has collected data (see #1 above) to show that a different ratio should be used. The value of 1 is conservative and will not err on the side of violating standards. This approach is very simple to apply because it places the entire burden of data collection and analysis solely upon permitted facilities. In terms of technical merit, it has the same characteristics of the previous approach. However, permitting authorities may be faced with difficulties in negotiating with facilities on the amount of data necessary to determine the ratio and the necessary quality control methods to assure that the ambient data are reliable.

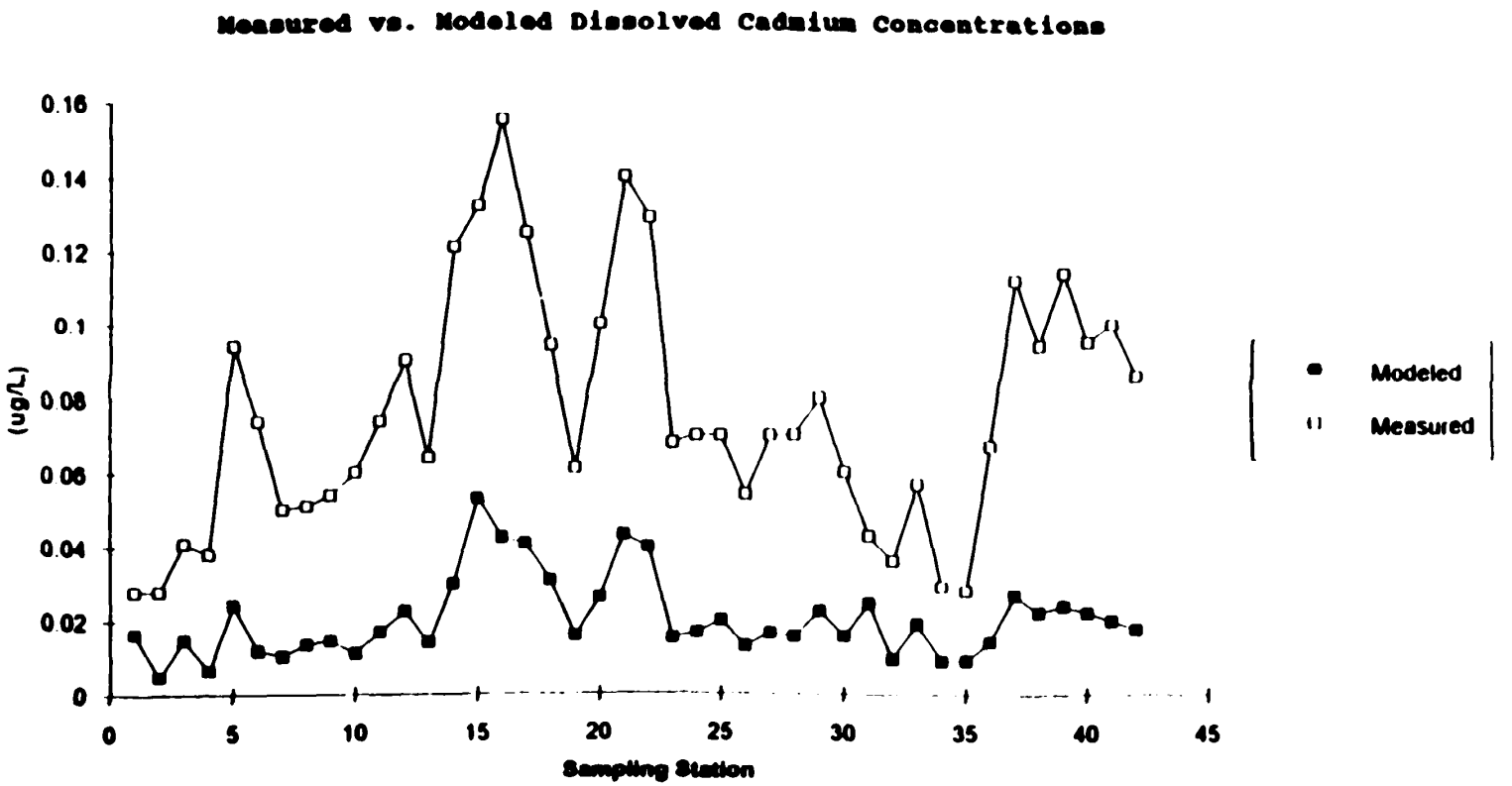
3. Use the historical data on total suspended solids (TSS) in receiving waterbodies at appropriate design flows and K_d values presented in the Technical Guidance Manual for Performing Waste Load Allocations. Book II. Streams and Rivers. EPA-440/4-84-020 (1984) to "translate" between (total recoverable) permits limits and dissolved metals in receiving water. This approach is fairly simple to apply. However, these K_d values are suspect due to possible quality assurance problems with the data used to develop the values. EPA's initial analysis of this approach and these values in one site indicates that these K_d values generally over-estimate the dissolved fraction of metals in ambient waters (see Figures following). Therefore, although this approach may not provide an accurate estimate of the dissolved fraction, the bias in the estimate is likely to be a conservative one.

EPA suggests that regulatory authorities use approaches #1 and #2 where States express their water quality standards in the dissolved form. In those States where the standards are in the total recoverable or acid soluble form, EPA recommends that no

translation be used until the time that the State changes the standards to the dissolved form. Approach #3 may be used as an interim measure until the data are collected to implement approach #1.



NMMA Exhibit 5



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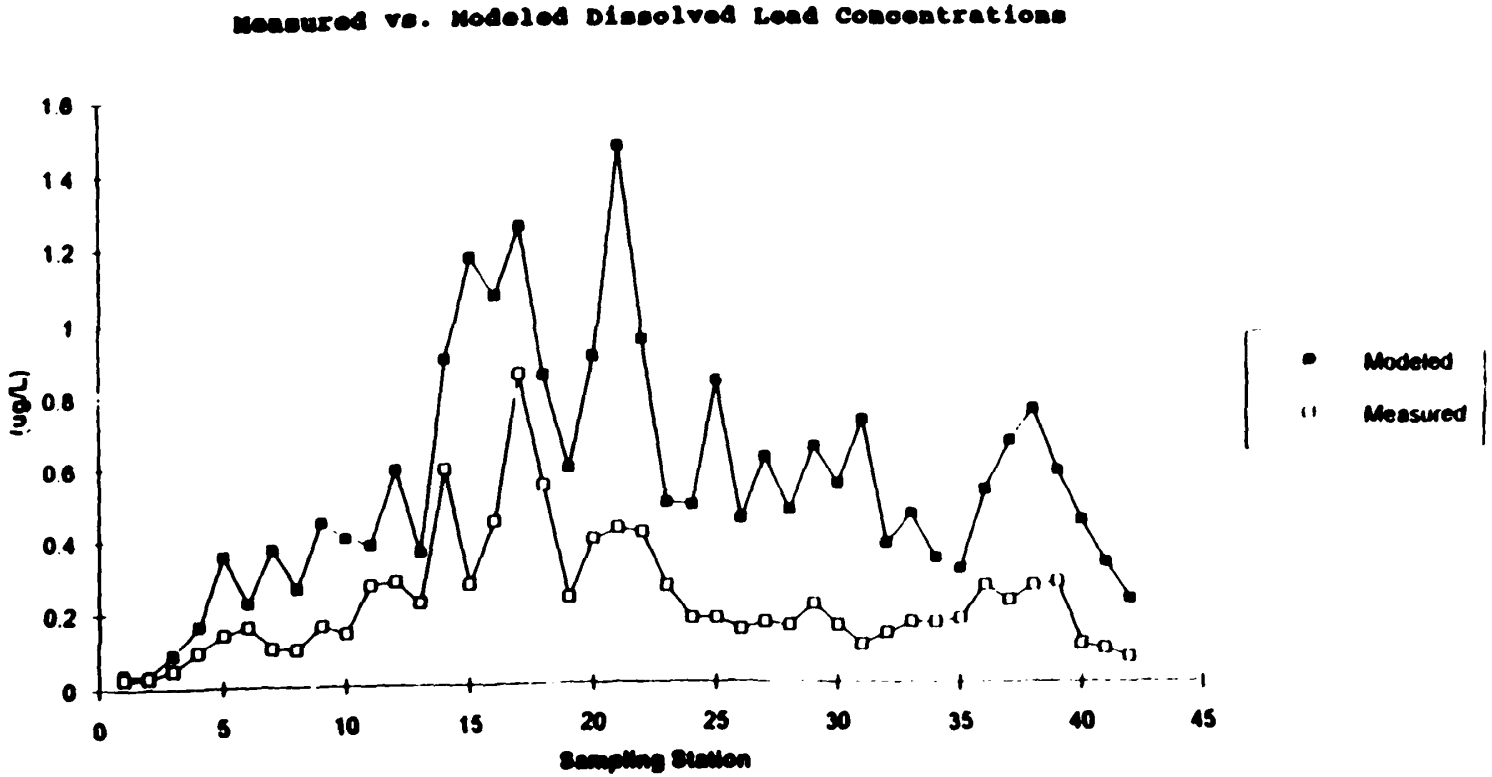

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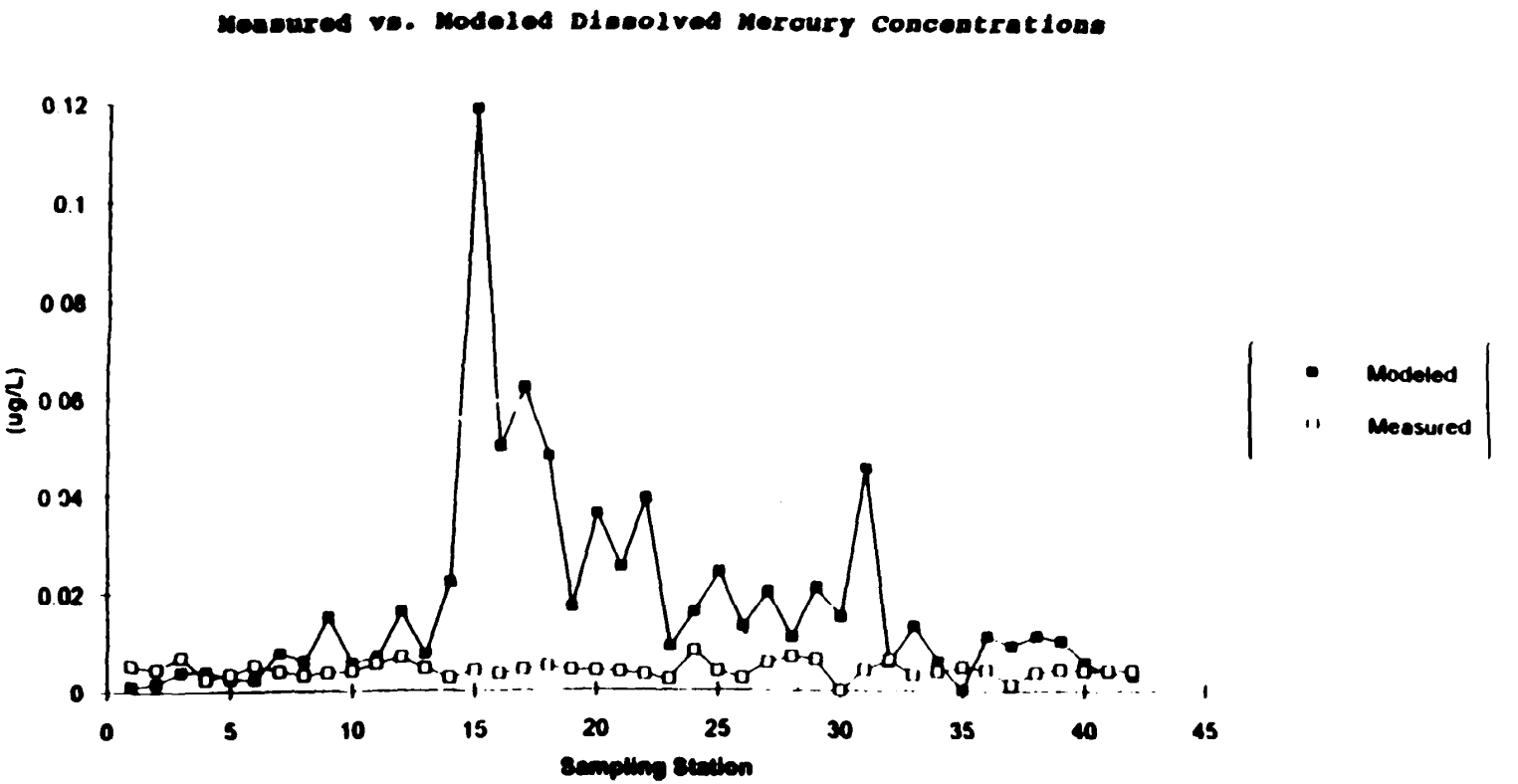

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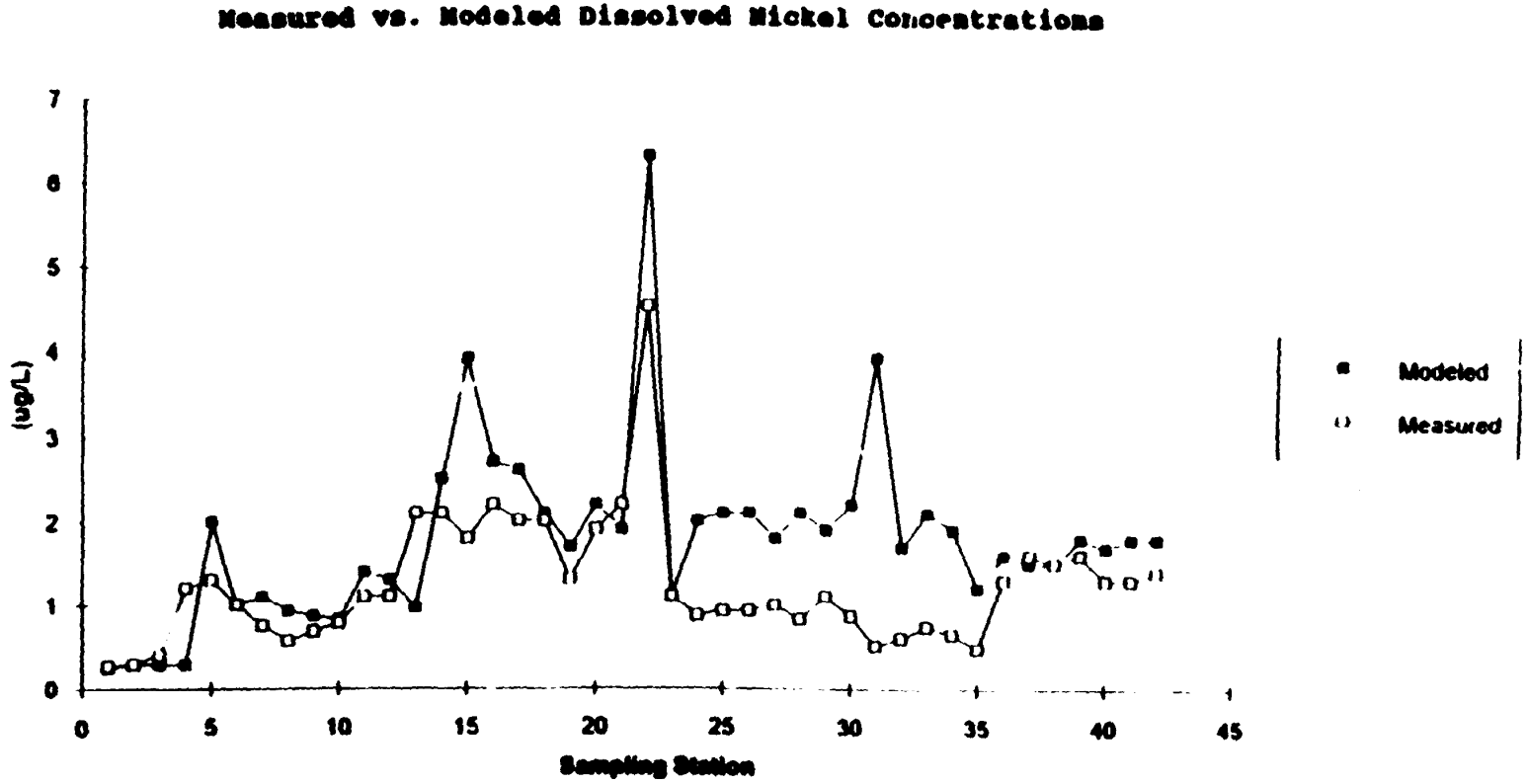

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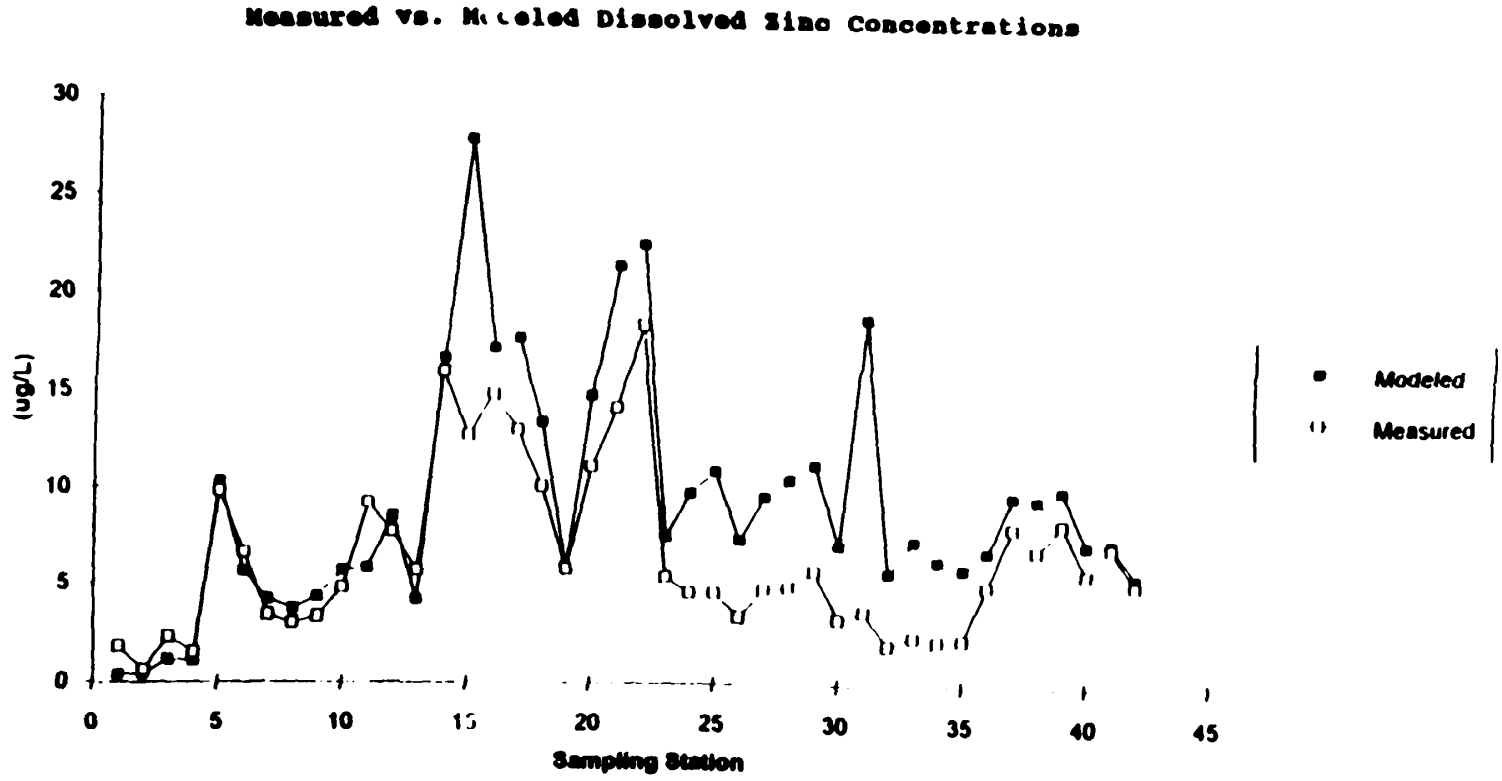
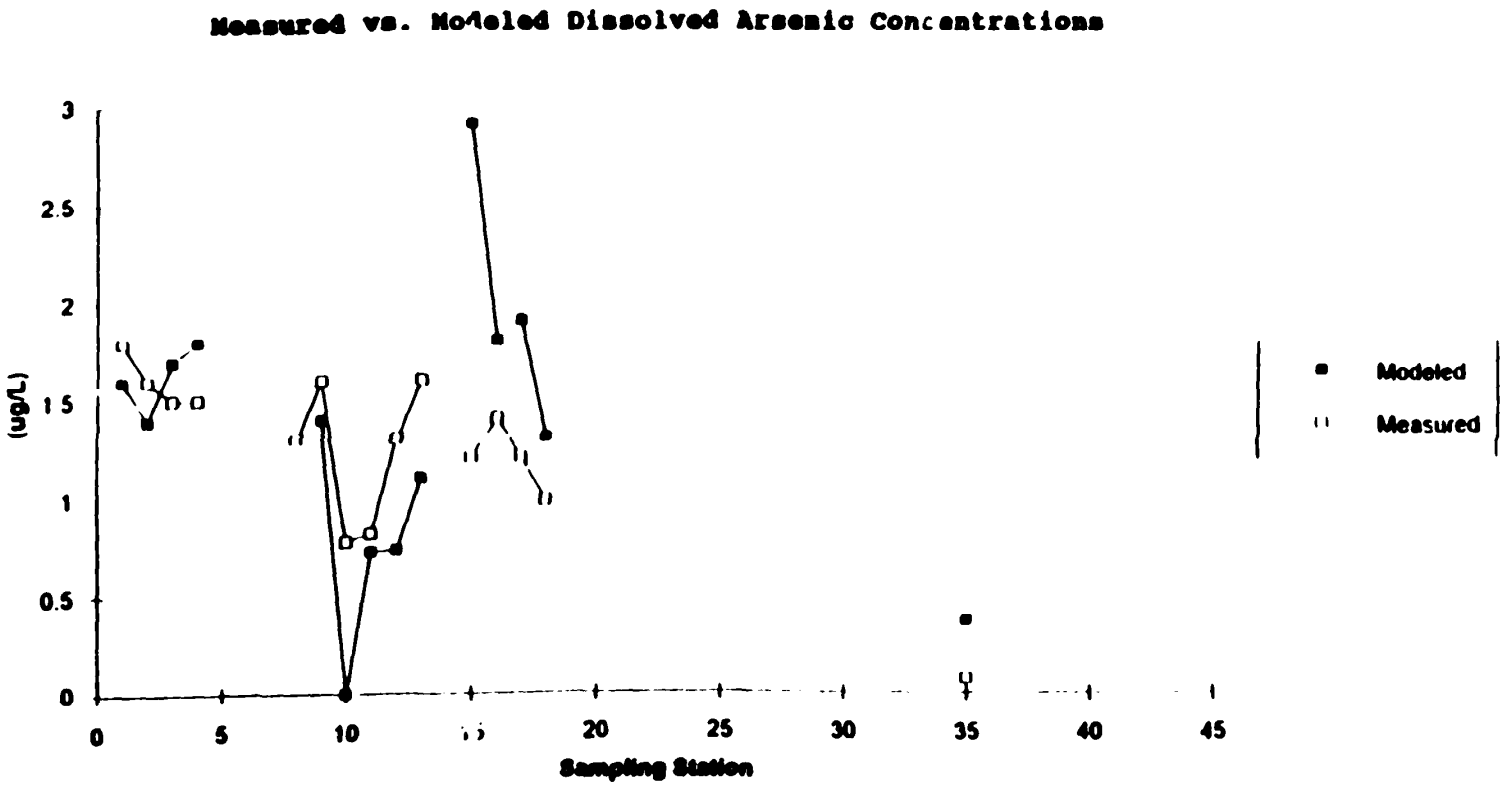


NMMA Exhibit 5



NMMA Exhibit 5

ATTACHMENT #4

GUIDANCE DOCUMENT ON CLEAN ANALYTICAL TECHNIQUES AND MONITORING
October 1993

Guidance on Monitoring

o Use of Clean Sampling and Analytical Techniques

Appendix B to the WER guidance document (attached) provides some general guidance on the use of clean techniques. The Office of Water recommends that this guidance be used by States and Regions as an interim step while the Office of Water prepares more detailed guidance.

o Use of Historical DMR Data

With respect to effluent or ambient monitoring data reported by an NPDES permittee on a Discharge Monitoring Report (DMR), the certification requirements place the burden on the permittee for collecting and reporting quality data. The certification regulation at 40 CFR 122.22(d) requires permittees, when submitting information, to state: "I certify under penalty of law that this document and all attachments were prepared under my direction or supervision in accordance with a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based on my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations."

Permitting authorities should continue to consider the information reported in DMRs to be true, accurate, and complete as certified by the permittee. Under 40 CFR 122.41(l)(8), however, as soon as the permittee becomes aware of new information specific to the effluent discharge that calls into question the accuracy of the DMR data, the permittee must submit such information to the permitting authority. Examples of such information include a new finding that the reagents used in the laboratory analysis are contaminated with trace levels of metals, or a new study that the sampling equipment imparts trace metal contamination. This information must be specific to the discharge and based on actual measurements rather than extrapolations from reports from other facilities. Where a permittee submits information

supporting the contention that the previous data are questionable and the permitting authority agrees with the findings of the information, EPA expects that permitting authorities will consider such information in determining appropriate enforcement responses.

In addition to submitting the information described above, the permittee also must develop procedures to assure the collection and analysis of quality data that are true, accurate, and complete. For example, the permittee may submit a revised quality assurance plan that describes the specific procedures to be undertaken to reduce or eliminate trace metal contamination.

Appendix B. Guidance Concerning the Use of "Clean Techniques" and QA/QC in the Measurement of Trace Metals

Recent information (Shiller and Boyle 1987; Windom et al. 1991) has raised questions concerning the quality of reported concentrations of trace metals in both fresh and salt (estuarine and marine) surface waters. A lack of awareness of true ambient concentrations of metals in saltwater and freshwater systems can be both a cause and a result of the problem. The ranges of dissolved metals that are typical in surface waters of the United States away from the immediate influence of discharges (Bruland 1983; Shiller and Boyle 1985,1987; Trefry et al. 1986; Windom et al. 1991) are:

Metal	Salt water (ug/L)	Fresh water (ug/L)
Cadmium	0.01 to 0.2	0.002 to 0.08
Copper	0.1 to 3.	0.4 to 4.
Lead	0.01 to 1.	0.01 to 0.19
Nickel	0.3 to 5.	1. to 2.
Silver	0.005 to 0.2	----------
Zinc	0.1 to 15.	0.03 to 5.

The U.S. EPA (1983,1991) has published analytical methods for monitoring metals in waters and wastewaters, but these methods are inadequate for determination of ambient concentrations of some metals in some surface waters. Accurate and precise measurement of these low concentrations requires appropriate attention to seven areas:

1. Use of "clean techniques" during collecting, handling, storing, preparing, and analyzing samples to avoid contamination.
2. Use of analytical methods that have sufficiently low detection limits.
3. Avoidance of interference in the quantification (instrumental analysis) step.
4. Use of blanks to assess contamination.
5. Use of matrix spikes (sample spikes) and certified reference materials (CRMs) to assess interference and contamination.
6. Use of replicates to assess precision.
7. Use of certified standards.

In a strict sense, the term "clean techniques" refers to techniques that reduce contamination and enable the accurate and precise measurement of trace metals in fresh and salt surface waters. In a broader sense, the term also refers to related issues concerning detection limits, quality control, and quality assurance. Documenting data quality demonstrates the amount of confidence that can be placed in the data, whereas increasing the sensitivity of methods reduce the problem of deciding how to

interpret results that are reported to be below detection limits.

This appendix is written for those analytical laboratories that want guidance concerning ways to lower detection limits, increase precision, and/or increase accuracy. The ways to achieve these goals are to increase the sensitivity of the analytical methods, decrease contamination, and decrease interference. Ideally, validation of a procedure for measuring concentrations of metals in surface water requires demonstration that agreement can be obtained using completely different procedures beginning with the sampling step and continuing through the quantification step (Bruland et al. 1979), but few laboratories have the resources to compare two different procedures. Laboratories can, however, (a) use techniques that others have found useful for improving detection limits, accuracy, and precision, and (b) document data quality through use of blanks, spikes, CRMs, replicates, and standards.

In general, in order to achieve accurate and precise measurement of a particular concentration, both the detection limit and the blanks should be less than one-tenth of that concentration. Therefore, the term "metal-free" can be interpreted to mean that the total amount of contamination that occurs during sample collection and processing (e.g., from gloves, sample containers, labware, sampling apparatus, cleaning solutions, air, reagents, etc.) is sufficiently low that blanks are less than one-tenth of the lowest concentration that needs to be measured.

Atmospheric particulates can be a major source of contamination (Moody 1982; Adeloju and Bond 1985). The term "class-100" refers to a specification concerning the amount of particulates in air (Moody 1982); although the specification says nothing about the composition of the particulates, generic control of particulates can greatly reduce trace-metal blanks. Except during collection of samples and initial cleaning of equipment, all handling of samples, sample containers, labware, and sampling apparatus should be performed in a class-100 bench, room, or glove box.

Nothing contained or not contained in this appendix adds to or subtracts from any regulatory requirements set forth in other EPA documents concerning metal analyses. The word "must" is used in this appendix merely to indicate items that are considered very important by analytical chemists who have worked to increase accuracy and precision and lower detection limits in trace-metal analysis. Some items are considered important because they have been found to have received inadequate attention in some laboratories performing trace-metal analyses.

Two topics that are not addressed in this appendix are:
1. The "ultraclean techniques" that are likely to be necessary when trace analyses of mercury are performed.
2. Safety in analytical laboratories.

Other documents should be consulted if these topics are of concern.

Avoiding contamination by use of "clean techniques"

Measurement of trace metals in receiving waters must take into account the potential for contamination during each step in the process. Regardless of the specific procedures used for collection, handling, storage, preparation (digestion, filtration, and/or extraction), and quantification (instrumental analysis), the general principles of contamination control must be applied. Some specific recommendations are:

a. Non-talc latex or class-100 polyethylene gloves must be worn during all steps from sample collection to analysis. (Talc seems to be a particular problem with zinc; gloves made with talc cannot be decontaminated sufficiently.) Gloves should only contact surfaces that are metal-free; gloves should be changed if even suspected of contamination.
b. The acid used to acidify samples for preservation and digestion and to acidify water for final cleaning of labware, sampling apparatus, and sample containers must be metal-free. The quality of the acid used should be better than reagent-grade. Each lot of acid must be analyzed for the metal(s) of interest before use.
c. The water used to prepare acidic cleaning solutions and to rinse labware, sample containers, and sampling apparatus may be prepared by distillation, deionization, or reverse osmosis, and must be demonstrated to be metal-free.
d. The work area, including bench tops and hoods, should be cleaned (e.g., washed and wiped dry with lint-free, class-100 wipes) frequently to remove contamination.
e. All handling of samples in the laboratory, including filtering and analysis, must be performed in a class-100 clean bench or a glove box fed by particle-free air or nitrogen; ideally the clean bench or glove box should be located within a class-100 clean room.
f. Labware, reagents, sampling apparatus, and sample containers must never be left open to the atmosphere; they should be stored in a class-100 bench, covered with plastic wrap, stored in a plastic box, or turned upside down on a clean surface. Minimizing the time between cleaning and using will help minimize contamination.
g. Separate sets of sample containers, labware, and sampling apparatus should be dedicated for different kinds of samples, e.g., receiving water samples, effluent samples, etc.
h. To avoid contamination of clean rooms, samples that contain very high concentrations of metals and do not require use of "clean techniques" should not be brought into clean rooms.
i. Acid-cleaned plastic, such as high-density polyethylene (HDPE), low-density polyethylene (LDPE), or a fluoroplastic, must be the only material that ever contacts a sample, except possibly during digestion for the total recoverable

measurement. (Total recoverable samples can be digested in some plastic containers.) Even HDPE and LDPE might not be acceptable for mercury, however.

3. All labware, sample containers, and sampling apparatus must be acid-cleaned before use or reuse.
   1. Sample containers, sampling apparatus, tubing, membrane filters, filter assemblies, and other labware must be soaked in acid until metal-free. The amount of cleaning necessary might depend on the amount of contamination and the length of time the item will be in contact with samples. For example, if an acidified sample will be stored in a sample container for three weeks, ideally the container should have been soaked in an acidified metal-free solution for at least three weeks.
   2. It might be desirable to perform initial cleaning, for which reagent-grade acid may be used, before the items are allowed into a clean room. For most metals, items should be either (a) soaked in 10 percent concentrated nitric acid at 50°C for at least one hour, or (b) soaked in 50 percent concentrated nitric acid at room temperature for at least two days; for arsenic and mercury, soaking for up to two weeks at 50°C in 10 percent concentrated nitric acid might be required. For plastics that might be damaged by strong nitric acid, such as polycarbonate and possibly HDPE and LDPE, soaking in 10 percent concentrated hydrochloric acid, either in place of or before soaking in a nitric acid solution, might be desirable.
   3. Chromic acid must not be used to clean items that will be used in analysis of metals.
   4. Final soaking and cleaning of sample containers, labware, and sampling apparatus must be performed in a class-100 clean room using metal-free acid and water. The solution in an acid bath must be analyzed periodically to demonstrate that it is metal-free.
   5. After labware and sampling apparatus are cleaned, they may be stored in a clean room in a weak acid bath prepared using metal-free acid and water. Before use, the items should be rinsed at least three times with metal-free water. After the final rinse, the items should be moved immediately, with the open end pointed down, to a class-100 clean bench. Items may be dried on a class-100 clean bench; items must not be dried in an oven or with laboratory towels. The sampling apparatus should be assembled in a class-100 clean room or bench and double-bagged in metal-free polyethylene zip-type bags for transport to the field; new bags are usually metal-free.
   6. After sample containers are cleaned, they should be filled with metal-free water that has been acidified to a pH of 2 with metal-free nitric acid (about 0.5 mL per liter) for storage until use. At the time of sample collection, the sample containers should be emptied and rinsed at least twice with the solution being sampled before the actual

sample is placed in the sample container.

k. Field samples must be collected in a manner that eliminates the potential for contamination from the sampling platform, probes, etc. Exhaust from boats and the direction of wind and water currents should be taken into account. The people who collect the samples must be specifically trained on how to collect field samples. After collection, all handling of samples in the field that will expose the sample to air must be performed in a portable class-100 clean bench or glove box.

l. Samples must be acidified (after filtration if dissolved metal is to be measured) to a pH of less than 2, except that the pH must be less than 1 for mercury. Acidification should be done in a clean room or bench, and so it might be desirable to wait and acidify samples in a laboratory rather than in the field. If samples are acidified in the field, metal-free acid can be transported in plastic bottles and poured into a plastic container from which acid can be removed and added to samples using plastic pipettes. Alternatively, plastic automatic dispensers can be used.

m. Such things as probes and thermometers must not be put in samples that are to be analyzed for metals. In particular, pH electrodes and mercury-in-glass thermometers must not be used if mercury is to be measured. If pH is measured, it must be done on a separate aliquot.

n. Sample handling should be minimized. For example, instead of pouring a sample into a graduated cylinder to measure the volume, the sample can be weighed after being poured into a tared container; alternatively, the container from which the sample is poured can be weighed. (For saltwater samples, the salinity or density should be taken into account when weight is converted to volume.)

o. Each reagent used must be verified to be metal-free. If metal-free reagents are not commercially available, removal of metals will probably be necessary.

p. For the total recoverable measurement, samples should be digested in a class-100 bench, not in a metallic hood. If feasible, digestion should be done in the sample container by acidification and heating.

q. The longer the time between collection and analysis of samples, the greater the chance of contamination, loss, etc.

r. Samples must be stored in the dark, preferably between 0 and 4°C with no air space in the sample container.

Achieving low detection limits

a. Extraction of the metal from the sample can be extremely useful if it simultaneously concentrates the metal and eliminates potential matrix interferences. For example, ammonium 1-pyrrolidinedithiocarbamate and/or diethylammonium diethyldithiocarbamate can extract cadmium, copper, lead,

nickel, and zinc (Bruland et al. 1979; Nriagu et al. 1993).
b. The detection limit should be less than ten percent of the lowest concentration that is to be measured.

Avoiding interferences

a. Potential interferences must be assessed for the specific instrumental analysis technique used and each metal to be measured.
b. If direct analysis is used, the salt present in high-salinity saltwater samples is likely to cause interference in most instrumental techniques.
c. As stated above, extraction of the metal from the sample is particularly useful because it simultaneously concentrates the metal and eliminates potential matrix interferences.

Using blanks to assess contamination

a. A laboratory (procedural, method) blank consists of filling a sample container with analyzed metal-free water and processing (filtering, acidifying, etc.) the water through the laboratory procedure in exactly the same way as a sample. A laboratory blank must be included in each set of ten or fewer samples to check for contamination in the laboratory, and must contain less than ten percent of the lowest concentration that is to be measured. Separate laboratory blanks must be processed for the total recoverable and dissolved measurements, if both measurements are performed.
b. A field (trip) blank consists of filling a sample container with analyzed metal-free water in the laboratory, taking the container to the site, processing the water through tubing, filter, etc., collecting the water in a sample container, and acidifying the water the same as a field sample. A field blank must be processed for each sampling trip. Separate field blanks must be processed for the total recoverable measurement and for the dissolved measurement, if filtrations are performed at the site. Field blanks must be processed in the laboratory the same as laboratory blanks.

Assessing accuracy

a. A calibration curve must be determined for each analytical run and the calibration should be checked about every tenth sample. Calibration solutions must be traceable back to a certified standard from the U.S. EPA or the National Institute of Science and Technology (NIST).
b. A blind standard or a blind calibration solution must be included in each group of about twenty samples.

c. At least one of the following must be included in each group of about twenty samples:
   1. A matrix spike (spiked sample; the method of known additions).
   2. A CRM, if one is available in a matrix that closely approximates that of the samples. Values obtained for the CRM must be within the published values.

The concentrations in blind standards and solutions, spikes, and CRMs must not be more than 5 times the median concentration expected to be present in the samples.

Assessing precision

a. A sampling replicate must be included with each set of samples collected at each sampling location.
b. If the volume of the sample is large enough, replicate analysis of at least one sample must be performed along with each group of about ten samples.

Special considerations concerning the dissolved measurement

Whereas the total recoverable measurement is especially subject to contamination during the digestion step, the dissolved measurement is subject to both loss and contamination during the filtration step.

a. Filtrations must be performed using acid-cleaned plastic filter holders and acid-cleaned membrane filters. Samples must not be filtered through glass fiber filters, even if the filters have been cleaned with acid. If positive-pressure filtration is used, the air or gas must be passed through a 0.2-um in-line filter; if vacuum filtration is used, it must be performed on a class-100 bench.
b. Plastic filter holders must be rinsed and/or dipped between filtrations, but they do not have to be soaked between filtrations if all the samples contain about the same concentrations of metal. It is best to filter samples from low to high concentrations. A membrane filter must not be used for more than one filtration. After each filtration, the membrane filter must be removed and discarded, and the filter holder must be either rinsed with metal-free water or dilute acid and dipped in a metal-free acid bath or rinsed at least twice with metal-free dilute acid; finally, the filter holder must be rinsed at least twice with metal-free water.
c. For each sample to be filtered, the filter holder and membrane filter must be conditioned with the sample, i.e., an initial portion of the sample must be filtered and discarded.

The accuracy and precision of the dissolved measurement should be

assessed periodically. A large volume of a buffered solution (such as aerated 0.05 N sodium bicarbonate) should be spiked so that the concentration of the metal of interest is in the range of the low concentrations that are to be measured. The total recoverable concentration and the dissolved concentration of the metal in the spiked buffered solution should be measured alternately until each measurement has been performed at least ten times. The means and standard deviations for the two measurements should be the same. All values deleted as outliers must be acknowledged.

Reporting results

To indicate the quality of the data, reports of results of measurements of the concentrations of metals must include a description of the blanks, spikes, CRMs, replicates, and standards that were run, the number run, and the results obtained. All values deleted as outliers must be acknowledged.

Additional information

The items presented above are some of the important aspects of "clean techniques"; some aspects of quality assurance and quality control are also presented. This is not a definitive treatment of these topics; additional information that might be useful is available in such publications as Patterson and Settle (1976), Zief and Mitchell (1976), Bruland et al. (1979), Moody and Beary (1982), Moody (1982), Bruland (1983), Adeloju and Bond (1985), Berman and Yeats (1985), Byrd and Andreae (1986), Taylor (1987), Sakamoto-Arnold (1987), Tramontano et al. (1987), Puls and Barcelona (1989), Windom et al. (1991), U.S. EPA (1992), Horowitz et al. (1992), and Nriagu et al. (1993).

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