THE Bay Foundation OF MORRO BAY
601 Embarcadero • Morro Bay, California 93442

DRINKING WATER WELL TESTING PROGRAM FOR THE CENTRAL COAST REGION

REQUEST FOR PROPOSALS
Due by 5:00 P.M.
Monday, January 16, 2023

I. INTRODUCTION

The Bay Foundation of Morro Bay (Bay Foundation) is issuing a Request for Proposals (RFP) to well-qualified contractors that can provide domestic well sampling and analytical testing of collected samples for the continuation of the existing Central Coast Drinking Water Well Testing Program[1] (Program). Proposals must address all services described in Exhibit A – Scope of Work.

II. APPLICATION INSTRUCTIONS

This section provides instructions for preparing and applying for this RFP. The section consists of two subsections: A) How to Submit and, B) What to Submit. It is important that contractors follow the Application Instructions to ensure their application will address the required elements. Contractors are reminded that once the application has been submitted to the Bay Foundation, any privacy rights as well as other confidentiality protections afforded by law with respect to the application package will be waived.

A. HOW TO SUBMIT

The deadline to submit applications is Monday, January 16, 2023 no later than 5:00 PM. Applicants must submit a complete application in an electronic searchable PDF or Microsoft Word format. Documents that are less than 10MB should be emailed to the following address below. Specify, “Central Coast Drinking Water Well Testing Program RFP Submittal” with the subject line. Documents that are 10MB or larger should be transferred to a USB Drive and mailed to the address listed below. The Bay Foundation will not accept applications submitted after the deadline.

Applicants are responsible for all costs of developing and submitting a bid package. Such costs cannot be charged to the Bay Foundation or included in any cost element of a contractor’s price offering.

[1] www.centralcoastwelltesting.org

Email:	mgrubbs@mbnep.org
Physical Mailing Address:	The Bay Foundation of Morro Bay Attn: Melodie Grubbs 601 Embarcadero, Suite 11 Morro Bay, CA 93442

If an applicant has a question as to the content or information requested in the RFP Notice, please contact the following staff (email preferred):

Melodie Grubbs, Executive Director
mgrubbs@mbnep.org
(805) 772-3834

B. WHAT TO SUBMIT

This section includes general information and a list of minimum submittal requirements.

GENERAL INFORMATION

Organization Type:
The RFP is directed to entities that demonstrate the ability to accomplish the work as described in this RFP, are not listed as debarred or suspended in the System for Award Management[2], and submit a complete application by the deadline.

Schedule:

Deadline to submit proposals	**January 16, 2023 (30 days from announcement.)**
Tentative deadline to select Contractor	**February 10, 2023**
Tentative contract start date	**March 10, 2023**
Contract Term	**Two years, with an additional extension based on performance and funding availability**

Available Funds and Distribution:

California Regional Water Quality Control Board, Central Coast Region (Central Coast Water Board) Resolution R3-2022-0015 allocated a total of $600,000 of the Central Coast Water Board's Central Coast Ambient Monitoring Program – Groundwater Assessment and Protection Program (CCAMP-GAP) Fund to continue the Central Coast Drinking Water Well Testing Program for approximately 3 years. This RFP is for a contract planned for a term of 2 years and budget of approximately $400,000, with the possibility of an extension based on performance and available funds. Only work specified in the executed agreement will be reimbursed and funds cannot be used for work performed prior to award and approval of the executed agreement. The Bay Foundation of Morro Bay Executive Director reserves the right to increase

[2] www.sam.gov

or decrease the funds awarded or reject all applications and make no awards under this announcement. Such changes may be necessary as a response to the quality of applications received or the amount of funds available. The Bay Foundation of Morro Bay is not required to award an agreement.

Project Area:

The project area is the central coast region[3] which includes all of Santa Cruz, San Benito, Monterey, San Luis Obispo, and Santa Barbara Counties, as well as the southern areas of Santa Clara County, and small portions of San Mateo, Kern, and Ventura Counties. Program work will emphasize areas of the central coast region with the highest density of underrepresented communities.

MINIMUM PROPOSAL SUBMITTAL REQUIREMENTS (1-6)

Potential contractors interested in submitting an application shall submit a complete application in a searchable PDF or Microsoft Word format containing the following elements:

1. **Project Name and Applicant information**

   - Application transmittal and title page shall clearly identify project name "Central Coast Drinking Water Well Testing Program."
   - Submitting contractor.
   - Legal Name on file with the Secretary of State and Federal Identification Number of the contractor as appropriate.
   - Designated contact person and/or Project Director, including name, physical address, phone number and email address.

2. **Scope of Work**

   A full scope of work is provided in Exhibit A. The scope of work includes the following components.
   - Program Management
   - Internal and external Program coordination and reporting
   - Quality Assurance / Quality Control
   - Field Sampling Activities
   - Analytical Testing of Samples
   - Data Transmittal and Management

3. **Budget**

   A budget sheet is provided in Exhibit B.
   - The application must include a completed budget sheet aligned with the activities described in the scope of work.

[3] Central Coast Region Boundary

4. Statement of Qualifications (SOQ)

Applications for this RFP shall include the following statement of qualifications (SOQ) components and information:

Professional Experience and References

- The applicant's professional experience in performing the specific tasks within the scope of work, with a description of professional experience and background of the organization in relation to water quality, water quality sampling and testing (with an emphasis on groundwater well and public/domestic water supply sampling and testing), public communication and project management and coordination. Please provide details of any current or previous efforts in the Central Coast Region relevant to the scope of work.
- Examples of completed or on-going work that illustrate effective implementation of water quality sampling, handling and testing, public communication, and project management and coordination. Include a list of references and contacts for each of the projects.
- A list of additional references with contact information and a description of the professional relationship with the applicant and any sub-contractors identified within the SOQ.

Personnel and Expertise

- A list of proposed personnel to be assigned to the project. The list should identify each person's professional experience and qualifications. The list should also include the description of professional experience and background of any sub-contractors. The percentage of time each person will spend on the project must be estimated and stated, and tasks in the scope of work under their responsibility should be identified.
- The SOQ must clearly identify the person that will be responsible for directing the team (Project Director). It is expected that technical personnel will be dedicated to the technical aspects of the project under the oversight of the Project Director such that technical staff are not also responsible for non-technical project management or administrative tasks.
- A description of any other background, training, skill, or experience relevant to the organization and/or personnel assigned to the project.

Capacity

- A statement of the applicant’s capacity to implement the project (i.e., the number of field sampling events and water quality analyses that can be implemented on a daily or weekly basis).
- The applicant and all sub-contractors must have sufficient capacity to implement field sampling and analytical testing according to the Scope of Work and QAPP.

Laboratory Certification

- Documentation of the laboratory’s State Water Resources Control Board Division of Drinking Water Environmental Laboratory Accreditation Program (ELAP) certification for drinking water analyses.
- A copy of the laboratory’s quality assurance manual subject to the requirements of Title 22, section 64815.
- Documentation of the laboratory’s Electronic Deliverable Format (EDF) capabilities.

- A list of the standard testing methods, holding times and reporting limits for the specified list of water quality parameters/constituents contained within the scope of work

5. RESUMES OF PROJECT DIRECTOR AND OTHER KEY PERSONNEL

6. LETTERS OF SUPPORT

- Three letters of support, with contact information and description of professional relationship to applicant.

SELECTION AND ADMINISTRATIVE PROCESS

The contractor will be selected on the basis of written responses to this RFP. Submittals will be evaluated based upon the completeness and depth of the information requested above under "Minimum Proposal Submittal Requirements." Submittals will also be evaluated based on the proposed budget relative to the proposed scope of work, as well as based on prospective contractor reliability as follows:

- Quality and relevance of completed and ongoing work;
- Demonstrated availability, reliability, and continuity of applicant's proposed staff and sub-consultants;
- Description of workload, organizational capacity and demonstrated ability to meet project requirements, tasks included in the scope of work and associated schedule;
- Past performance on Water Board funded or other drinking water and wastewater projects; and
- Letters of Support and References.

Attachments

A. Scope of Work
B. Budget Sheet

1. OVERVIEW:

A. _____ (Contractor) agrees to provide the following services to the Bay Foundation of Morro Bay (Bay Foundation) as described herein:

Contractor shall fulfill the roles of Project Manager and Quality Assurance (QA) Manager, Sampling Coordinator, and Sampling Technician for the Quality Assurance Project Plan (QAPP) and Sampling and Analysis Plan (SAP) Version 1.2 (May 2021). The Contractor shall provide project management, field sampling, analytical testing, and data management services for the implementation of a voluntary drinking water well sampling project in the Central Coast Region.

B. The services shall be performed throughout rural areas within the jurisdiction of the Central Coast Water Board with an emphasis on underrepresented communities. Underrepresented communities include but are not limited to Disadvantaged Communities (DACs), Severely Disadvantaged Communities (SDACs), Economically Distressed Areas (EDAs), Tribes, Environmentally Disadvantaged Communities (EnvDACs), and members of Fringe Communities.[1]

C. Public notification of this project will be conducted via an accompanying outreach and education project to be implemented by the State Water Resources Control Board (State Water Board) and the California Regional Water Quality Control Board, Central Coast Region (Central Coast Water Board), (collectively referred to herein as the Water Boards) in coordination with other third-party contractors pursuant to a separate Agreement. The project will typically be implemented county by county and phasing of the outreach and education activities will be coordinated with the Contractor pursuant to this Agreement to facilitate the stepwise implementation of the field sampling activities.

[1] Disadvantaged Community: a community with an annual median household income that is less than 80% of the Statewide annual median household income (Public Resources Code section 80002(e)); Severely Disadvantaged Community: a community with a median household income of less than 60% of the Statewide average. (Public Resources Code section 80002(n)); Economically Distressed Area: a municipality with a population of 20,000 persons or less, a rural county, or a reasonably isolated and divisible segment of a larger municipality where the segment of the population is 20,000 persons or less, with an annual median household income that is less than 85% of the Statewide median household income, and with one or more of the following conditions as determined by the department: (1) financial hardship, (2) Unemployment rate at least 2% higher than the Statewide average, or (3) low population density. (Water Code section 79702(k)); Tribes: federally recognized Indian Tribes and California State Indian Tribes listed on the Native American Heritage Commission's California Tribal Consultation List; EnvDACs: CalEPA designates the top 25 percent scoring census tracts as DACs. Census tracts that score the highest 5 percent of Pollution Burden scores, but do not have an overall CalEnviroScreen score because of unreliable socioeconomic or health data, are also designated as DACs (refer to the CalEnviroScreen 3.0 Mapping Tool or Results Excel Sheet); Fringe Community: communities that do not meet the established DAC, SDAC, and EDA definitions, but can show that they score in the top 25 percent of either the Pollution Burden or Population Characteristics score using the CalEnviroScreen 3.0

D. The services shall be provided during the Contractor's normal business hours. However, consideration should be given to members of the public who wish to participate in this project but can't do so during normal business hours.

E. The Project Representatives during the term of this Agreement will be:

Bay Foundation of Morro Bay	Contractor
Attention: Melodie Grubbs Executive Director	Attention:
Address: 601 Embarcadero, Suite 11 Morro Bay, CA 93442	Address:
Phone: (805) 772-3834	Phone:
e-mail: MGrubbs@mbnep.org	e-mail:

The parties may change their Project Representative upon providing ten (10) business days written notice to the other party. Said changes shall not require an Amendment to this Agreement.

The Central Coast Water Board is not a party to this Agreement, but serves as a technical advisor to the Bay Foundation and Contractor.

Central Coast Water Board
Attention: Julia Dyer Senior Environmental Scientist (Specialist)
Address: 895 Aerovista Place, Suite 101 San Luis Obispo, CA 93401
Phone: (805) 542-4624
e-mail: Julia.Dyer@waterboards.ca.gov

2. WORK TO BE PERFORMED:

A. Background and Goals

The Bay Foundation is pursuing the continuation of the Central Coast Drinking Water Well Testing Program[2] (Program) within the Central Coast Region with an emphasis on areas at higher risk for groundwater impacts and underrepresented communities. The project is intended to inform the implementation of similar projects in the State of California where there are significant drinking water problems affecting domestic wells and small water systems.

[2] www.centralcoastwelltesting.org (English) / www.ccanalisisdepozos.org (Español)

There are approximately 44,000 private domestic wells in the Central Coast Region. Many of these domestic wells are more susceptible to pollution given their shallow depths and rural locations within or adjacent to areas subject to intensive land uses (e.g. irrigated agriculture). Between October 2018 and February 2022, the Program tested a total of 420 individual wells. Of the total 420 wells tested, 40% show at least one exceedance of a primary Maximum Containment Level (MCL) and/or the Program's interim screening level of 10 ug/L for hexavalent chromium. Nitrate, hexavalent chromium, and arsenic are the most commonly detected contaminants[3]. Consequently, many communities living within rural areas of the Central Coast Region who do not get their drinking water from a public water system are at risk of drinking groundwater that does not meet safe drinking water standards.

The primary objectives of the Central Coast Drinking Water Well Testing Program are to:

1. Provide free water quality sampling and analytical services (along with supporting information) to domestic well and small water system well owners so they can make informed decisions about the safety of their drinking water.
2. Provide the Bay Foundation, Water Boards, local agencies and general public with regional-scale groundwater quality data associated with unregulated sources of drinking water.

The groundwater and drinking water quality data generated from this project and subsequent projects will be used to 1) inform well owners about the safety of their drinking water and inform the general public and local and state agencies about groundwater quality (via upload of data to GeoTracker[4] and available to the public to view and download via GAMA GIS[5] and technical reports), 2) serve as a baseline for future sampling efforts to evaluate groundwater quality over time, and 3) help water agencies to evaluate and prioritize source control and replacement water supply efforts. The data generated from this Program and follow-up projects will be used to identify Water Board priorities inform/substantiate Water Board actions and evaluate the effectiveness of those actions over time.

B. Tasks and Deliverables

Task 1. Project Management

[3] More details are provided in the Central Coast Drinking Water Well Testing Program Update, April 21 – 22, 2022 Item No. 3 Attachment 2
[4] GeoTracker https://geotracker.waterboards.ca.gov/
[5] Groundwater Ambient Monitoring and Assessment Program Groundwater Information System https://gamagroundwater.waterboards.ca.gov/gama/gamamap/public/Default.asp

1.1 Internal and external coordination and documentation of project implementation consistent with the tasks as described herein and subtasks below.

1.2 Internal Project Coordination: The Contractor shall coordinate project tasks with designated personnel and provide oversight for project implementation, including program staffing, training, implementation and follow-up as necessary to ensure program timing, consistency, and effectiveness.

1.3 External Project Coordination: The Contractor shall coordinate with the Bay Foundation, Water Boards, and other program partners to ensure efficient implementation of the Program and to maximize Program participation:
- 1.3.1 Provide ongoing evaluations of project implementation and performance, coordinate outreach, evaluate response to outreach, discuss and modify program implementation, etc.
- 1.3.2 Coordinate logistics before, during, and after localized geographically focused Program implementation, generally by county.
- 1.3.3 Participate in Program kick off coordination meeting(s) prior to initiating sampling in a local area.

1.4 Reporting:
- 1.4.1 Submit reports in PDF searchable electronic format including the following:
  - 1.4.1.1 Report and documentation as described in Task 3 Invoices and Deliverables of project implementation as described throughout this Scope of Work,
  - 1.4.1.2 Documentation of external project coordination via meeting attendance lists, minutes and action items for each meeting or conference call associated with the reporting period.

Note: Portions of any information or reports associated with this contract containing well ownership or location information, or that could facilitate the nexus between this information and the project specific GeoTracker Global ID number, shall be clearly labeled as "CONFIDENTIAL" and be maintained as such.

Task 2. Quality Assurance Project Plan, Sampling and Analysis Plan, and Field Safety Procedures.

The Contractor shall be responsible for any necessary revisions or updates to the Quality Assurance Project Plan (QAPP), Sampling and Analysis Plan (SAP)Version 1.2 (May 2021), and Field Safety Procedures (November 25, 2020)[6]. All revisions and updates to the QAPP and SAP will be made in general accordance with the US EPA Requirements for Quality Assurance Project Plans

[6] Tetra Tech Memo, *Central Coast Domestic Well Sampling Project: Field Sampling Element Re-Start* Lindsey (November 25, 2020)

EPA QA/R-5, 3/01[7]. The SAP and revisions or updates are based in-part on the laboratory's Laboratory Operations and Quality Assurance Plan per the Water Boards Division of Drinking Water Environmental Laboratory Accreditation Program (ELAP) requirements governing the collection, handling and testing of water quality samples (i.e., Title 22, section 64815).

Revisions or updates to the project specific QAPP, SAP, and/or Field Safety Procedures shall be submitted, in PDF searchable electronic format, to the Bay Foundation Contract Manager for review and approval prior to finalizing the revised document.

2.1. Any revisions or updates to the QAPP and SAP shall include protocols and standard forms/templates as necessary for the following:
   - 2.1.1. Project participant request for analyses (RFA), coordination and tracking,
   - 2.1.2. Sampling procedures,
   - 2.1.3. Chain of custody (COC),
   - 2.1.4. Sample preservation & holding time.
   - 2.1.5. Quality assurance and quality control for project implementation, field sampling, analytical testing, and data management,
   - 2.1.6. Field and laboratory analyses (using standard methods via laboratory certified by State Water Board Environmental Laboratory Accreditation Program for drinking water analyses) for the following parameters:

1,2,3-Trichloropropane
Arsenic
Nitrate (as N)
Perchlorate
Chromium, Hexavalent
pH (field)
Specific Conductance (field)
Total Dissolved Solids
Total Alkalinity as CaCO3
Potassium
Magnesium
Calcium
Sodium
Chloride
Sulfate (SO4)
Carbonate as CO3
Hydroxide
Bicarbonate as HCO3

[7] https://www.epa.gov/quality/epa-qar-5-epa-requirements-quality-assurance-project-plans

2.1.7. On a limited basis, additional sampling parameters not identified in 2.1.6 may be required to assess drinking water quality in specific areas. The specific parameter(s) will be identified for a specific drinking water well(s) and approved by the Bay Foundation Contract Manager and Contractor, in advance.

2.1.8. Perform field sampling and analytical testing in accordance with approved United States Environmental Protection Agency (USEPA) sampling and analytical methods for drinking water and certified through a California Environmental Laboratory Accreditation Program (ELAP). Conduct periodic audits, at least annually, of the analytical methods specified in Table 11 to ensure that samples are representative of drinking water. Analytical Methods and Reporting Limits for Field and Laboratory Parameters (QAPP and SAPP Version 1.2 (May 2021)).

2.1.9. Additional field sampling parameters are required to document that the well and plumbing appurtenances have been sufficiently purged prior to sample collection.[8]

2.2. The Field Safety Procedures describe actions to protect both participants and the field technicians from health and safety risks that may be encountered during implementation of the project, including potential exposure to COVID-19 and degraded air quality during active wildfires. The Contractor shall update Field Safety Procedures as necessary.

Task 3. Invoices and Deliverables

The Contractor shall submit, to the Bay Foundation's Contract Manager for approval, reports in PDF searchable electronic format containing the results of the work performed in accordance with this Scope of Work along with the associated invoices.

3.1. Reports shall include information as described in the subtasks below and enumerate the activities conducted within the reporting period with a clear nexus to project invoicing for specific tasks and deliverables. Invoices shall

[8] The Contractor shall ensure that drinking water samples characteristic of the raw and untreated groundwater supply are collected by qualified personnel, as indicated per the following. Groundwater samples shall be collected by qualified personnel (e.g., consultant, technician, etc. with applicable training and experience) using proper sampling methods, chain of custody, and quality assurance/quality control protocols. Groundwater samples shall be collected at or near the well head before the pressure tank and prior to any treatment. In cases where this is not possible, the water sample shall be collected from a sampling point as close to the pressure tank as possible, or from a cold-water spigot located before any filters or water treatment systems. Prior to collecting samples, the water shall be run to purge the well or water system until field parameters (e.g., pH, water temperature, specific conductance, oxidation-reduction potential [ORP] and dissolved oxygen) stabilize within an acceptable range as defined within the SAP.

provide an accounting of expenditures within each report clearly enumerating the dollar amount and percentage of funds expended for the reporting period and project to-date with respect to the total available project funding.

3.1.1. Documentation of program implementation and effectiveness with any lessons learned and proposed modifications,
3.1.2. Documentation of the laboratories ongoing ELAP certification,
3.1.3. Documentation of dates of RFA, and field sampling scheduling and implementation,
3.1.4. Documentation of data upload to GeoTracker,
3.1.5. Documentation of results mail out,
3.1.6. Site information/data,
3.1.7. Access agreements,
3.1.8. Field sampling forms,
3.1.9. Chain of custody,
3.1.10. Laboratory analytical data sheets, and
3.1.11. Compilation of project participant contact information, well location and water quality data in a tabular electronic format; format to be developed by contractor in coordination with the Central Coast Water Board's Contract Manager.

Reports will not be considered final until accepted and approved by the Central Coast Water Board's Contract Manager.

The Central Coast Water Board Contract Manager shall use the reports to evaluate and approve invoices. Within two (2) weeks of receipt of the reports and associated invoices, the Central Coast Water Board's Contract Manager shall submit comments to the Contractor as needed to rectify any deficiencies.

Task 4. Individual Well Sampling

Scheduling and implementation of sampling, analysis, and data management pursuant to QAPP and SAP. The Contractor shall provide qualified personnel to implement and coordinate project related tasks consistent with the QAPP and SAP. In general, drinking water sampling will be implemented in phases, based on county.

4.1. Coordinate with project participants:
4.1.1 Establish and maintain dedicated point(s) of contact to include with project notification outreach materials (to be prepared and disseminated by the Water Boards, local agency, or other third party); this includes local or toll-free phone number(s), and
4.1.2 Schedule and confirm field sampling visits with project participants within five (5) working days of requests to participate in the project and implement field sampling activities within twenty (20) working days. Deviations from this schedule may be approved in coordination

with the contract manager. For example, when project participants are identified outside of the focused sampling area and must be sampled at a later date to reduce cost. When possible, the Contractor shall schedule multiple field sampling visits for sites in relative proximity to each other to maximize project efficiency.

4.2. Collection of site information and data:
- 4.2.1 Site address and number of parcels/residences served by well (include assessors' parcel numbers served by well as available),
- 4.2.2 Participant name and contact information including mailing address (if different from site address), phone number and email address,
- 4.2.3 Determination of well location coordinates (i.e., latitude and longitude with respect to NAD 83 datum) via handheld GPS or other appropriate method. Ensure GPS accuracy, calibration and operation.
- 4.2.4 Depth to groundwater if well construction/operation allows measurement,
- 4.2.5 Well construction details as available (i.e. date of construction, size, depth, screen interval or Department of Water Resources well completion report),
- 4.2.6 Site conditions, surrounding land-use activities, septic system proximity to well, etc.
- 4.2.7 Photo documentation of wellhead, adjacent area and sample collection location.

4.3. Conduct field sampling activities:
- 4.3.1 Meet with project participants, or their designated representative, for sampling,
- 4.3.2 Complete access agreements, field forms, chain of custody, etc.,
- 4.3.3 Implement and document field sample collection, preservation and holding activities, including measurement of field parameters,
- 4.3.4 Assign the Field Point Name as specified in the QAPP and SAP in section 6.4.3 Chain of Custody.
- 4.3.5 Collect and document other site information,
- 4.3.6 Coordinate with laboratory personnel for sample delivery/pickup per chain of custody procedures, and
- 4.3.7 Central Coast Water Board staff will accompany project field sampling personnel on at least two days to observe and document implementation of field sampling tasks.

4.4. Analytical testing of samples:
- 4.4.1 Conduct and document laboratory analytical testing and QA/QC consistent with the QAPP, SAP, and other relevant quality assurance protocols and documents.

4.5. Data transmittal and management:

4.5.1 Upload of water quality data and well location coordinates to GeoTracker[9] by the laboratory via Electronic Deliverable Format (EDF) within five (5) working days of completing water quality analyses.

4.5.2 Maintenance of well owner/participant name, locational information, and field data confidentiality via Field Point Name assigned per 4.3.4.

4.5.3 Within five (5) working days of completing the water quality analyses, transmit (via e-mail or regular mail) water quality results to project participants with supporting information provided by the Central Coast Water Board,

4.5.3.1 Supporting information to the water quality results shall include information that alerts the participant to results that exceed a Primary Maximum Contaminant Level (MCL) or the Program's interim screening level of 10 ug/L for hexavalent chromium.

4.5.4 Track and resubmit water quality results packages as necessary due to mail delivery failure.

Note: Central Coast Water Board staff or third party will follow up with a phone call to participants for wells that exceed a drinking water standard to confirm receipt and understanding of data.

[9] Project Name: Central Coast Domestic Well Sampling Project, Global ID: T10000010346

Exhibit B – Budget Sheet

CONSULTANT NAME: _____

A. Well Sampling Cost Table

Parameter Analysis	Cost Per Sample
1. 1,2,3-Trichloropropane	
2. Arsenic	
3. Nitrate (as N)	
4. Perchlorate	
5. Chromium, Hexavalent	
6. pH (field)	
7. Specific Conductance (field)	
8. Total Dissolved Solids	
9. Total Alkalinity as CaCO3	
10. Potassium	
11. Magnesium	
12. Calcium	
13. Sodium	
14. Chloride	
15. Sulfate (SO4)	
16. Carbonate as CO3	
17. Hydroxide	
18. Bicarbonate as HCO3	
19. Total Analytical Cost per Well (Sum of Lines 1-18)	
	Cost Per Well
Well Sampling Implementation and Data Delivery	
20. Scheduling and Coordination of Field Sampling	
21. Field Sampling Activities	
22. Data upload to GeoTracker	
23. Transmittal of results to project participants	
24. Total Imp. and Data Delivery Cost per Well (Sum of Lines 20-23)	
Total Estimated Well Sampling Cost	
25. Total Cost Per Well (Lines 19 & 24)	
26. Estimated Number of Wells	
27. Well Sampling Cost Subtotal (Line 25 X 26)	
28. Quality Assurance / Quality Control (QA/QC) Wells[1]	
29. Estimated Number of QA/QC Wells	
30. QA/QC Well Sampling Cost Subtotal (Line 28 X 29)	
31. "No Show" Appointments[2]	
32. Estimated Number of "No Show" Appointments	
33. "No Show" Appointments Cost Subtotal (Line 31 X 32)	

[1] QA / QC Wells are collected at a rate of 5% (1 in 20) of the total samples collected.
[2] Occasionally, wells are scheduled, and the project participant is a 'no show'.

34. Additional Sampling Parameters (not identified in 1-18). Not to exceed line item budget.	$15,000
35. Total Estimated Well Sampling Cost (Sum of Lines 27, 30, 33, and 34)	

B. Project Management Cost Table

Budget Items	Hourly Rate	Estimated Hours	Estimated Cost
Project Management			
36. Project Management			
37. QAPP and SAP Updates[3]			
38. Preparation of Invoices and Deliverables			
39. Total Project Management Costs (Sum of Lines 36 - 38)	-	-	

Total Estimated Project Cost (Sum of Lines 35 & 39) _____

[3] Quality assurance and quality control costs associated with sample collection, handling and analytical testing (e.g., blanks, spikes, calibration checks, replicates, splits, chain-of-custody, etc.) per the Water Board Division of Drinking Water ELAP required Laboratory Operations and Quality Assurance Plan shall be included in the total estimated well sampling cost.

QUALITY ASSURANCE PROJECT PLAN

CENTRAL COAST DOMESTIC WELL SAMPLING FOR THE CENTRAL COAST REGIONAL WATER QUALITY CONTROL BOARD

Version 1.2

May 2021

Submitted to:

Mr. Matthew Keeling
Central Coast Regional Water Quality Control Board
895 Aerovista Place, Suite 101
San Luis Obispo, CA 93401-7906

Prepared by:

Tetra Tech, Inc.
3201 Airpark Dr., Ste. 108
Santa Maria, CA 93455

Funding Provided by the Central Coast Regional Water Quality Control Board, Groundwater Assessment and Protection (GAP) Program via a June 20, 2017 Funding Agreement with The Bay Foundation of Morro Bay

SECTION A – PROJECT MANAGEMENT

1.0 TITLE AND APPROVAL SHEET

Quality Assurance Project Plan
Central Coast Domestic Well Sampling for the Central Coast Regional Water Quality Control Board

Prepared by:
Tetra Tech, Inc.

This Quality Assurance Project Plan (QAPP) directs the collection and analysis of groundwater samples, and is intended to ensure the chemical and observational data generated by Tetra Tech Inc. (Tetra Tech), is of known quality for its intended purpose.

Matthew Keeling, Central Coast Regional Water Board (CCRWQB) Domestic Well Sampling Project Manager

Signature _____ Date 1/31/18

Karen Worcester, CCRWQB, Quality Assurance Officer

Signature _____ Date 1/31/18

Alex Van Dellen, Tetra Tech, Project Manager

Signature _____ Date 2/15/18

Tim Tringali, Tetra Tech, Quality Assurance Manager

Signature _____ Date 2/15/18

David Terz, Fruit Growers Laboratory (FGL), Quality Assurance Director

Signature _____ Date 2/15/18

2.0 TABLE OF CONTENTS

APPENDICES

LIST OF FIGURES

LIST OF TABLES

3.0 DISTRIBUTION LIST

Tetra Tech will manage the distribution of this QAPP, establishing a document control system to ensure (1) that all parties holding a controlled copy of this QAPP receive revisions/addenda promptly, and (2) that outdated material is removed from circulation. Personnel in possession of controlled copies are responsible for further distribution of amended material within their organization.

The individuals listed in Table 1 compose the primary distribution list for this QAPP.

Table 1
Primary Distribution List for the Quality Assurance Project Plan

Name	Organization	Email
Julia Dyer	CCRWQCB	Julia.Dyer@waterboards.ca.gov
Mark Davis	CCRWQCB	Mark.Davis@waterboards.ca.gov
Mary Hamilton	CCRWQCB	Mary.Hamilton@waterboards.ca.gov
Melissa Daugherty	CCRWQCB	Melissa.Daugherty@waterboards.ca.gov
Rusty Lindsey	Tetra Tech	Rusty.Lindsey@tetratech.com
Tim Tringali	Tetra Tech	Tim.Tringali@tetratech.com
Tracy L Proefrock	FGL	tracyp@fglinc.com
Glenn Olson	FGL	glenno@fglinc.com

4.0 PROJECT ORGANIZATION

4.1 PROJECT TEAM

The Central Coast Region has contracted with Tetra Tech to perform domestic well sampling, analysis, and reporting. The Central Coast Regional Water Quality Control Board (CCRWQCB) will fulfill the role of Contract Manager and Quality Assurance (QA) Officer. Tetra Tech will fulfill the roles of Project Manager, Quality Assurance Manager, Sampling Coordinator, and Sampling Technician. FGL will fulfill the role of environmental laboratory and Data Manager under subcontract to Tetra Tech. The project organization, including individuals assigned for each of the roles described above, is presented in Table 2 and Figure 1.

Table 2
Project Roles and Responsibilities

Name	Organization	Role	General Responsibilities
Julia Dyer	CCRWQCB	Contract Manager	• Provide contract oversight • Ensure project goals are met
Mark Davis	CCRWQCB	Technical Liaison	• Provide contract oversight and technical support to Contract Manager.
Mary Hamilton Melissa Daugherty	CCRWQCB	QA Officer(s)	• Ensure that QA requirements are met as stated in this QAPP • Addresses QA issues with the Contract Manager
			•
Rusty Lindsey	Tetra Tech	Project Manager	• Oversee monitoring and reporting • Ensure that adequate personnel and equipment are available to perform tasks in this QAPP
Tim Tringali	Tetra Tech	QA Manager	• Review field and lab data to per this QAPP • Address field and lab QA issues
Monica SanNicolas	Tetra Tech	Intake Coordinator	• Perform project participant intake • Schedule sampling events • Perform data entry
Emily Jensen Wolf	Tetra Tech	QA Manager and Sample Coordinator	• Perform project participant intake • Schedule sampling events • Perform data entry
Glenn Olsen	FGL	Lab QA Director	• Ensure proper receipt and handling, analysis and reporting of samples • Address laboratory QA issues
Tracy Proefrock	FGL	Data Manager	• Perform GeoTracker uploads

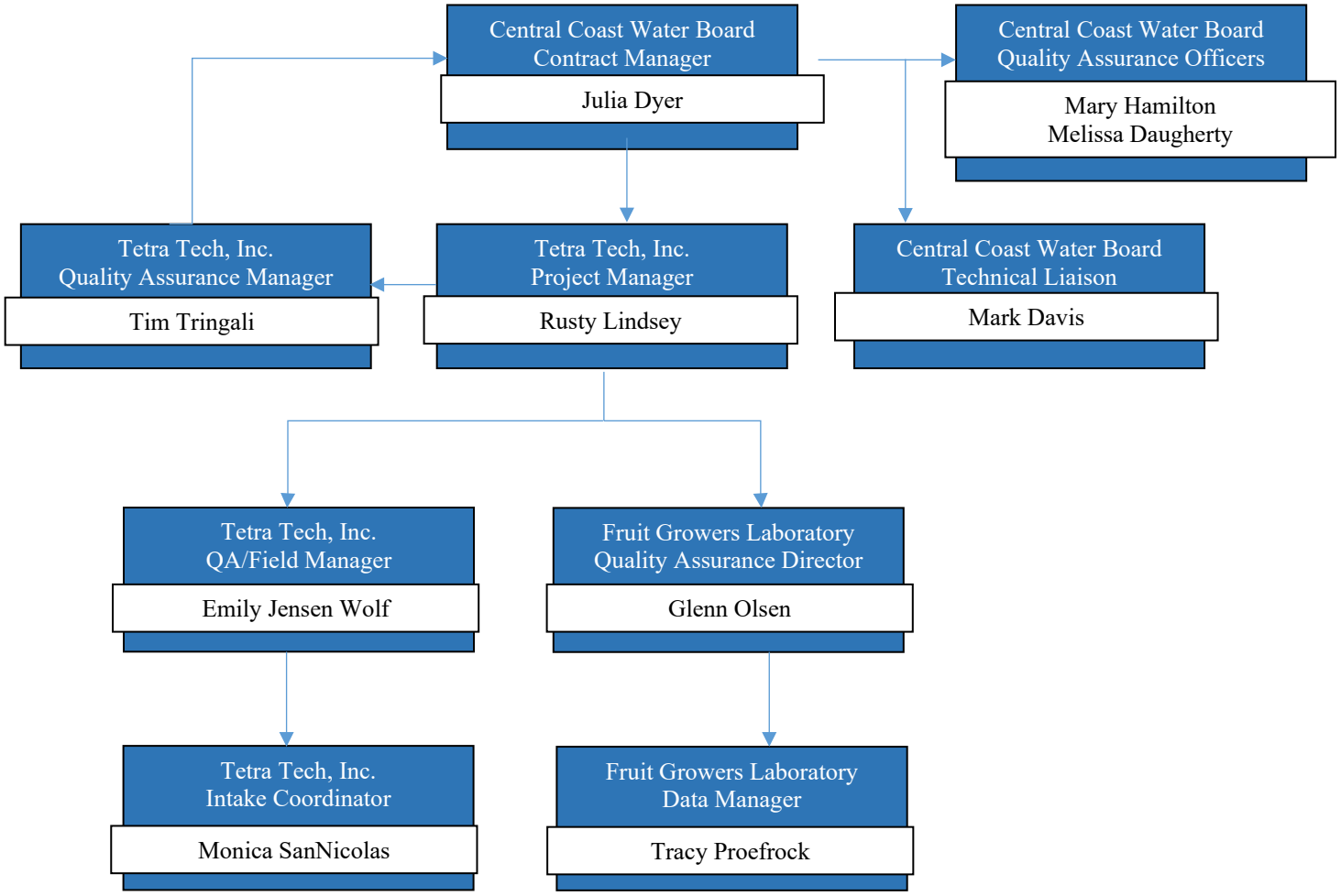


Figure 1
Central Coast Domestic Well Sampling Project Management Structure

4.2 QUALITY ASSURANCE MANAGER

Tim Tringali (Tetra Tech) is the Project Quality Assurance (QA) Officer. The Project QA Officer will review all laboratory data for compliance with the quality assurance/quality control (QA/QC) requirements specified in this QAPP, and ensure that the data is properly managed in the electronic database for the program. Although the Project QA Officer is responsible for communicating with the Project Manager, the Project QA Officer will operate independently in regard to mandating that all parties meet the QA/QC requirements in this QAPP. The Project QA Officer will review and assess all procedures during the life of the contract against QAPP requirements, and will report all findings to the Project Manager, including all requests for corrective action(s). The Project QA Officer may temporarily stop all actions, including field sampling and laboratory analyses, if there are significant deviations from required practices or if there is evidence of a systematic failure. The Project QA Officer must immediately contact the Contract Manager to determine whether immediate corrective actions can be implemented to reinitiate work.

4.3 QAPP AMENDMENTS

The QAPP shall be amended whenever there is a change to sampling, analytical, QA/QC procedures, or when deemed necessary by Tetra Tech or the CCRWQCB. The initial version of this QAPP will be referred to as Version 1.0. Minor edits to this QAPP will result in an increase of "0.1" to the version number (e.g., 1.1, 1.2, etc.). Major edits to this QAPP will result in an increase to the whole number (e.g., 2.0, 3.0, etc.). QAPP amendments will be listed in Table 3 and certified by the Tetra Tech Project Manager and the QA Manager. The Tetra Tech Project Manager will be responsible for distributing draft copies for review and a final copy to the CCRWQCB for signature, as well as distribution of the final version to appropriate project team members.

Table 3
QAPP Amendments Log

Amendment No.	Date	Amendment Description	Version No.	Project Manager Signature
1	9/10/2018	Revised Appendix A, Project Participant Database, to reflect changes to the intake questions found in *Intake Step 2* of the database. Similar adjustments were made to the bulleted questions found in Section 6.2 of this QAPP.	1.1	
2	5/13/2021	Multiple revisions including updating personnel (Tables 1, 2 and Figure 1), correcting an error in the RPD calculation, revising appendices (revise Appendix C and remove Appendix H)	1.2	
3				
4				
5				
6				
7				

5.0 PROBLEM DEFINITION/BACKGROUND

Regulatory oversight of water resources along the Central Coast of California is administered by the CCRWQCB. The footprint regulated by the CCRWQCB extends from the Pacific Ocean inland approximately 50 miles, from Santa Cruz to Carpinteria. Groundwater basins within the Central Coast region have some of the most widespread and severe nitrate pollution in the state. It is estimated there are 44,000 private domestic wells in the Central Coast Region. Many domestic wells and small water systems are located in rural areas or small communities, within or adjacent to areas subject to intensive irrigated agricultural land uses. These wells are at a higher risk of contamination, especially in disadvantaged communities, given their shallow depths. Furthermore, these high-risk communities are the least likely to have access to information on the quality of the water they are drinking. Nitrate contaminated drinking water is a top priority of the CCRWQCB; therefore, the CCRWQCB is pursuing domestic well outreach and sampling within the Central Coast Region.

6.0 PROJECT/TASK DESCRIPTION

The primary objectives of the Central Coast Domestic Well Sampling Project are to:

1. Provide free groundwater sampling and analytical services to domestic well and small non-public water system well owners so they can make informed decisions about the safety of their drinking water; and

2. Provide the Water Boards, local agencies, and general public with regional-scale groundwater quality data associated with unregulated sources of drinking water.

To accomplish these objectives, Tetra Tech and/or FGL will be:

- Collecting project participant information;
- Coordinating well sampling;
- Sampling domestic wells and documenting location-specific information;
- Analyzing groundwater grab samples;
- Uploading analytical results to GeoTracker GAMA (Groundwater Ambient Monitoring and Assessment Program); and
- Distributing and communicating analytical results to project participants.

Figure 2 – Project Description Flowchart, outlines the basic project task sequence and responsible staff associated with Sections 6.2 through 6.8.

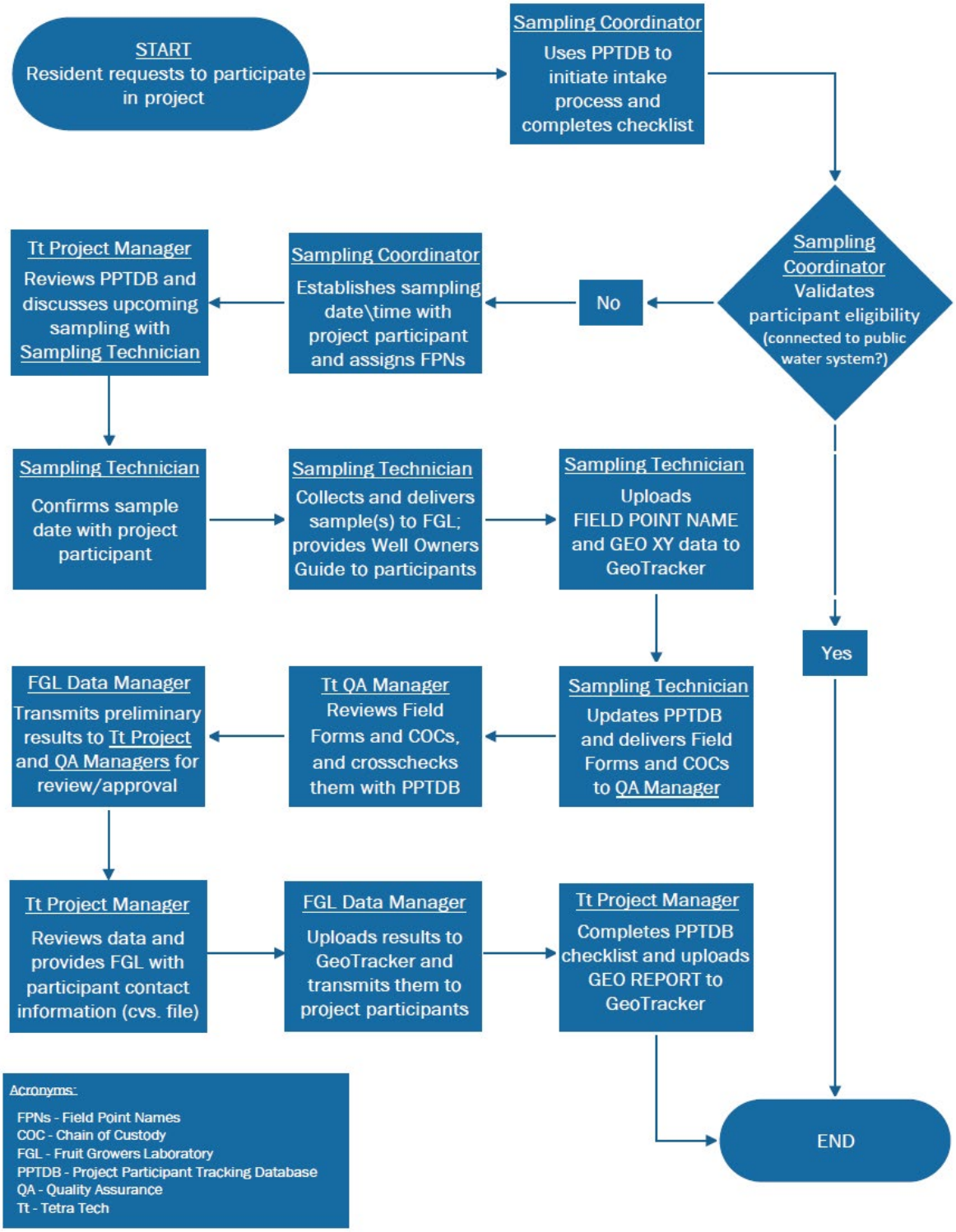


Figure 1
Project Description Flowchart

6.1 GEOGRAPHIC AREA OF SAMPLING

While specific sampling locations are unknown at this time due to the voluntary nature of the program, the general sampling area includes the jurisdiction of the CCRWQCB (Figure 3).

Image Source: University of California, Division of Agriculture and Natural Resources

Figure 3
Project Boundaries

6.2 PROJECT PARTICIPANT COORDINATION AND TRACKING

A dedicated toll-free phone number (1-844-613-5152) and website with associated QR code (https://sites.google.com/view/ccgroundwater) will be distributed for use on outreach and education materials so prospective project participants can get additional information and request sampling. Sampling Coordinators will screen and in-board prospective participants and schedule field sampling with qualifying participants. If no one is available to answer the phone, a recording in both English and Spanish will prompt the caller to leave a message. Messages will be returned within three business days and a field sampling visit with project participants will be scheduled within five business days from receipt of the call.

Each potential project participant will be asked a series of questions to help determine qualification for the free well sampling, and if they qualify, additional questions will be asked to facilitate well sampling. Project participant information will be documented and tracked within a Microsoft Excel database, also referred to as the *Project Participant and Tracking Database* (hereafter PPTDB; Appendix A). The database will also be used to document and track scheduling and implementation of sampling activities, sampling Field Point

Names, preparation and submittal/upload of GeoTracker Electronic Data Deliverable (EDD) files (using the Electronic Deliverable Format, or EDF [see Section 6.7]) and the transmittal of results to project participants. The PPTDB will be used as the primary project deliverable along with GeoTracker uploads for invoicing purposes.

To qualify for the free sampling, a project participant must obtain their drinking water from a private domestic well, a local small water system well with 2-4 residential connections, or a state small water system well with 5-14 residential connections. One or more of the following questions may be asked to verify that the potential project participant qualifies for free sampling:

- Do you know where your drinking water comes from?
- Do you receive your drinking water from a well?
- Do you receive any kind of water bill?
- Do you know how many homes, buildings, businesses, etc., are served by the well you use?
- Do you recall receiving an annual water quality report summarizing the quality of your drinking water?
- Is your well affiliated with a church, school, or business?
- Is there a location at or near your well where a sample may be collected (e.g., spigot, y-valve, blow-off, etc.)?

If a potential project participant qualifies for free well sampling, the following project participant information will be obtained to the maximum extent practicable, and documented within the PPTDB:

- Date of request;
- Name of requestor;
- Requestor's contact information (i.e., mailing address, phone number, email address);
- Alternate point of contact (name, phone number, email address);
- Number of wells;
- Physical address of well(s);
- Number of parcels/residences served by each well;
- Well construction information (i.e., date of construction, size, depth, screen interval);
- Well completion report (document provided by the Department of Water Resources);
- Presence/absence of water treatment devices (if present, document type and location);

- Presence/absence of a septic system;
- Proximity of wells to a septic system;
- Planned date of sampling;
- Does project participant want or need to be onsite for sampling; and
- Are there any access issues (e.g., locked gates, dogs, etc.).

Participants may also request well sampling through an online signup process via the following website:

https://sites.google.com/view/ccgroundwater

The process will work as follows:

1. Participant accesses the site, fills out an electronic questionnaire (consistent with PPTDB in-boarding questions) and request to participate.
2. Web-based system populates a spreadsheet with responses to questionnaire (including contact information) and sends email to Tetra Tech Sampling Coordinator regarding new request to participate.
3. Tetra Tech Sampling Coordinator logs into the site and integrates the spreadsheet into the PPTDB for processing.
4. Sampling Coordinator contacts participant as needed to complete the in-boarding and scheduling process.

Once it has been determined that a potential project participant qualifies for the free sampling and the aforementioned participant and well information has been obtained, well sampling will be scheduled. Assuming that the project participant schedule allows, the scheduling will be such that samples are collected within one month of the request.

At this time, GeoTracker Field Point Names (FIELD_PT_NAME) will be tentatively assigned in the PPTDB for the individual wells to be sampled. See Section 6.7, Table 4 for Field Point Name conventions (note: field-generated quality control [QC] samples submitted to the laboratory for analyses require special Field Point Name and/or Sample ID conventions to differentiate them from standard well water quality samples). Field Point Names need to be entered in GeoTracker following sampling activities as a place holder for the subsequent upload of global position system well coordinates (GEO_XY) and analytical data for each well. In the event that a Field Point Name is not applied in sequence (e.g., a well is not sampled as planned), it can either be skipped or applied in subsequent sampling events. Skipped Field Point Names will also be tracked in the PPTDB with appropriate notations.

6.3 SAMPLING PREPARATIONS

Prior to mobilizing to a well site, the Tetra Tech Project Manager will review the PPTDB with the Sampling Technician to:

- Discuss each location and combined daily sampling locations with the Sampling Technician (one sampling technician will be responsible for collecting samples) to review the trip plan and identify and address any potential issues of concern;

- Review running list of used, assigned and available GeoTracker Field Point Names (FIELD_PT_NAME) and assign Field Point Names as needed to the next set of wells to be sampled that are associated with qualified participants as identified in the PPTDB. Sampling Technicians will have a running list of Field Point Names for use in the field. Most Field Point Names will be pre-assigned as part of the participant in-boarding or sampling preparation process as recorded in the PPTDB, but the Sampling Technician will have the ability to add new participants (i.e., sample additional wells) and assign Field Point Names while in the field by using the next available Field Point Name on the list; and

- Determine if additional sampling kits need to be requested from FGL to accommodate scheduled sampling events.

Field equipment will be calibrated prior to sampling activities, as well as at the end of the day to monitor measurement drift. Equipment calibration is explained in detail in Section 15.1 of this document.

6.4 SAMPLING ACTIVITIES

This section summarizes sampling activities procedures including: 1) field data collection; 2) sample collection; and 3) preparation of chain-of-custody (COC) forms.

6.4.1 Field Data Collection

Prior to each sampling event, the Sampling Coordinators will issue a copy of the PPTDB (Appendix A) to the Sampling Technician(s). The PPTDB will be used to contact the project participant in advance of sampling, plan for well sampling and to track Field Point Names.

In the field, the Sampling Technician will prepare the *Central Coast Domestic Well Sampling Field Sampling Form* (hereafter, Field Sampling Form; Appendix B) for each well sampled. All field measurements will be recorded in the field using the form. At a minimum, the following sample-specific information will be provided for each sample collected (see Section 6.7, Table 4 - GeoTracker GAMA Electronic Deliverable Format (EDF) fields for specified conventions; EDF fields are identified by capitalized text in parentheses):

- Unique Field Point Name (FIELD_PT_NAME) for each well sampled. With the exception of quality control samples as discussed below and within Table 4, the Field Point Name will double as the Sample ID (SAMPID);

- Well location coordinates (GEO_XY) (e.g., latitude/longitude);

- Field Point Class (FIELD_PT_CLASS) (i.e., description of well type and water system size);

- Field Point Description (FIELD_PT_DESC) identifying type of sampling point (i.e., well head or distribution system) with additional information provided on the sampling form as needed to clarify location (e.g., hose bib, tap, faucet, etc. located on north side of house, etc.);

- Quality Control (QC) sample type prepared/collected at this location (if appropriate); and
- Date and time(s) of collection (i.e., military time).

6.4.2 Sample Collection

Sample collection will generally include: 1) site preparation and observations, 2) well stabilization, and 3) sample collection. As noted in section 6.4.1, all field observations and activities will be documented on the Field Sampling Form, which is included as Appendix B.

6.4.2.1 Site Preparation and Observations

Site preparation and observations will include the following:

1. Document the Sampling Technician(s) present;
2. Document Field Point Names and Sample IDs to be applied to wells and collected samples:
3. Document the date and time of well sampling;
4. Document weather conditions at the time of sampling;
5. Document and photograph the surrounding land use;
6. Document and photograph the well condition and location;
7. Identify and photograph well purge water discharge location before and after purging activities;
8. Document and photograph the specific sample location at each well;
9. Document the type and location of any treatment systems;
10. Document the latitude/longitude of the well (note any issues with data collection such as tree cover, minimal satellite coverage, etc.; if issues, collect offset measurements from fixed points such as a building, etc.);
11. Apply labels to each bottle; labels will document the Field Point Name and Sample ID, the date/time the sample was obtained, analytical method, and Sampling Technician who collected the sample.

When the well construction details are known, calculate and record the casing volume (water column) of the well using the following equation:

$$V = \pi r^2 h(7.48)$$

where: π = 3.14
r = radius of the well in decimal feet (inches/12)
h = the height of the water column in the well in feet (bottom depth – static water elevation)
7.48 = conversion from cubic feet to gallons.

6.4.2.2 Well Stabilization

Well stabilization will be performed according to the following protocol and be documented on the Field Sampling Form:

1. Identify appropriate well purge discharge location in coordination with project participant. Location and method of discharge shall be selected to prevent runoff and erosion.

2. Start the well pump, and record the start time;

3. Purge the well of two to three casings of water to ensure groundwater samples are representative of conditions within the aquifer. If the well volume is not known, pump an adequate volume of water to achieve stabilization in accordance with the criteria below in Step 5;

4. While purging the well, collect and record water quality measurements for pH, specific conductivity, and dissolved oxygen (DO), every 2 to 3 minutes using a field meter;

5. Well stabilization should occur after two to three well casings are purged and when successive readings of pH and specific conductivity vary by no more than the following (dissolved oxygen can also be used to assess stability). If the construction details of the well are not known, water quality measurements will be recorded every 2 to 3 minutes until two consecutive readings are within the range of 'stabilization':

    a. ± 0.1pH units;

    b. ± 3% micro Siemens per centimeter (µS/cm), specific conductivity; and

    c. ± 1 milligram/liter (mg/L), DO.

6. Cleanup well purge area as needed.

6.4.2.3 Sample Collection

When possible, groundwater samples should be collected at the well head before the pressure tank and distribution system. All samples will be collected prior to any type of treatment (e.g., water softeners, reverse osmosis, etc.). In some cases, it may be necessary to collect samples at a location other than directly from the well head. Some well heads are configured such that effluent piping is buried underground and plumbed directly into the home or basement. Other wells are constructed without a sampling point (e.g., spigot, y-valve, blow-off, etc.), further prohibiting sample collection at the well head. In cases where samples cannot be collected at the well head, Sampling Technicians will select and document a sampling location that is prior to any treatment devices and most representative of the aquifer supplying water to the project participant.

Sample collection will be performed according to the following protocol:

1. Once stabilized according to the procedures described in Section 6.4.2.2, rinse a large steel bucket two times with water pumped from the well, then fill bucket;

2. Quickly fill all sample containers with water from the bucket, while also preventing any loss of preservative, and seal and place the containers within a cooler containing ice;

3. Decontaminate the stainless steel bucket and field equipment using the following procedures:

    a. Place the bucket and the sampling meter in a plastic bin designated for equipment decontamination.

    b. Use Alconox and deionized water to wash each item. Rinse each item with deionized water three times to remove Alconox.

    c. Capture all wash/rinse water and dispose off-site to the sanitary sewer.

4. Complete the COC for the samples collected (one per participant; can include multiple wells); and

5. Verify that all fields of the Field Sampling Form are completed and note any data gaps before leaving the location.

Each sample will be clearly labeled with the Field Point Name and Sample ID as outlined in Table 4. With the exception of QC duplicate samples generated in the field, the Sample ID will be the same as the Field Point Name. Field and equipment blank QC samples generated in the field and submitted to the laboratory for analyses under COC will use a standardized Field Point Name and Sample ID throughout the project.

All samples will be checked for a tight seal, and placed in plastic bags. Samples will be stored in coolers and completely filled with ice (either in Ziploc bags or tied garbage bags) to ensure the samples maintain a temperature below 6 degrees Celsius (˚C) throughout shipping. Samples will be handled to minimize analyte loss or contamination. The following procedures will be used to prevent bottle breakage and cross-contamination:

- Bubble wrap or foam pouches will be used to keep glass bottles from contacting one another;
- All samples will be transported inside hard plastic coolers; and
- Coolers will be taped shut and sealed with COC seal.

Note: due to the 48-hour holding time for nitrate (as N), samples must be delivered to the Satellite Laboratory by 3:00 PM and no more than 32 hours after collection to the Santa Paula Laboratory. **The laboratory must be notified in advance of any shipments sent on Friday for delivery on Saturday**. See Sections 11.0 and 12.0 for additional information regarding sample handling and COC procedures.

6.4.3 Chain of Custody

The COC procedures require that possession of samples be traceable from the time the samples are collected until submittal of analytical results. One COC form will be filled out per well owner and may include multiple wells. Project participants with multiple wells on the same property can be combined on one COC. Field Point Names will be included on the COC form and act as the identifier for individual wells and provide the nexus to project participants as tracked in the PPTDB (note: COC forms will not contain participant or well location information). The Sampling Technician will retain custody of samples from the point of sample collection to the point of shipment to FGL. A COC form will accompany the samples at all times. The COC form will be consistent with the sample label, and will indicate the analyses to be performed, number of containers, sample volume, preservatives and container type for each sample. All sample shipments will be accompanied by the COC form that identifies the contents of the cooler. The original COC form will accompany the shipment and a copy will be retained by the Sampling Technician

and be submitted to the Tetra Tech QA Manager along with the associated Field Sampling Forms for review along with the forthcoming analytical results. COC forms will be placed in a plastic zip lock bag and taped to the inside of the plastic cooler lid.

Sample naming (SAMPID) on the COC forms and sample bottles will be consistent with the following example for a well with an assigned Field Point Name of CCDW1 (see Table 4 for more detailed information regarding Field Point Name and Sample ID naming conventions):

- Sample ID: CCDW1 (same as Field Point Name);
- Field Duplicate Sample ID: CCDW1DUP (associated with a well with a Field Point Name and Sample ID of CCDW1 for the other sample); and
- QC Samples will all use the following for the Field Point Name and Sample ID, and be tracked by sampling date in association with the COC and the field sampling form;
  - Field Blank: QCFB
  - Equipment Blank: QCEB.

See section 12.0 for addition information regarding COC requirements and procedures.

6.5 LABORATORY DOCUMENTATION

For each sample analyzed, FGL will provide the Tetra Tech Project Manager and QA Manager with the following information within three business days of completing the analyses:

- Field Point Name:
- Sample ID;
- Date of sample receipt;
- Dates of extraction and analysis (if appropriate);
- Analytical method(s);
- Method detection limit (if appropriate);
- Reporting limit (if appropriate); and
- Measured value of the analyte or parameter.

In addition, FGL will provide results from all laboratory QC procedures (e.g., blanks, duplicates, spikes, reference materials, etc.) and the Field Point Names and Sample IDs associated with each analytical sample batch. Upon completion of the QA Manager's review of all laboratory results, FGL will be notified that the data is acceptable for upload to GeoTracker GAMA and distribution to the project participant.

The FGL Data Manager will mail test results to the project participant within five business days of completing the analyses and QA data review along with supporting information (see Section 6.8 for additional information).

6.6 DATA REVIEW AND PROCESSING

Following completion of the daily well sampling activities, the Sampling Technician will do the following:

1. Incorporate the field data into the PPTDB,
2. Upload Field Point Names and well coordinates (GEO_XY) to GeoTracker, and
3. Compile and provide the QA Manager with the completed Field Sampling Forms and associated photo-documentation, and copies of the COC forms.

The QA Manager will review the completed Field Sampling and COC forms for completeness and cross check them with the updated PPTDB. Upon completion of the QA Manager's review, the following activities will be implemented:

1. The QA Manager documents any errors or inconsistencies and coordinate updates/revisions, as appropriate;
2. The FGL Data Manager posts results and QC data for Tetra Tech Project and QA Managers review;
3. The Project and QA Manager reviews results and QC data, and cross check them with the PPTDB and associated Field Sampling and COC forms;
4. The Project Manager provides the FGL Data Manager with a .csv file containing the project participant contact information (i.e., email address, physical address, and contact name) associated with each Field Point Name to facilitate data transmittal to project participants;
5. The FGL Data Manager will create and upload the results EDD to GeoTracker after they are approved by the Project and QA Manager;
6. The Project Manager will create and upload GEO REPORT EDD file to GeoTracker; and
7. FGL will transmit the sampling results and supporting information package to project participants.

The above activities will be tracked and documented in the PPTDB by the Project Manager.

6.7 GEOTRACKER DATA UPLOAD

The Sampling Technicians will upload Field Point Names and well location data (i.e., latitude and longitude) to GeoTracker GAMA following the completion of daily sampling activities. This step needs to be completed before FGL can upload the sampling results EDF to GeoTracker. The Project Manager will also upload a single pdf document via a GEO_REPORT EDD file compiling all field sampling related documents for each sampling event, including COC forms, field sampling forms, photographs, etc. All data uploaded to GeoTracker GAMA will be done using the appropriate EDF Electronic Data Deliverable (EDD) requirements pursuant to the guidelines and restrictions found at the following SWRCB website:

http://www.waterboards.ca.gov/water_issues/programs/ust/electronic_submittal/docs/edf_gr_v1_2i.pdf

All fields in the EDD file should be completed as necessary to ensure data uploads are consistent and accurate. The required fields for GeoTracker GAMA are described in Table 4.

Table 4
GeoTracker GAMA Electronic Deliverable Format Fields

Data Field	Description
Global ID (Global_ID)	A project specific associative Global ID of **T10000010346** has been assigned for this project. Individual wells sampled as part of the project will be differentiated and tracked via unique Field Point Names as described below.
Field Point Name (FIELD_PT_NAME) Note: must be limited to 10 characters.	The following Field Point Name convention will be used for each well and used on the chain-of-custody and for EDF EDD reporting purposes: CCDW#, where "#" represents numbering sequence 1, 2, 3, etc. up to 9999 with first residence/well sampled starting with 1, and; CCDW#W# for residences or local/state small water systems with multiple wells, where the second "W#" represents a well numbering sequence of W1, W2, etc. up to W9 (e.g., the fourth residence/system sampled as part of the overall project that has two wells would have Field Point Names of CCDW4W1 and CCDW4W2) A unique Field Point Name is required for field-derived QC samples, other than duplicates (see Sample ID below regarding duplicates), submitted to the laboratory under COC for analyses. The following conventions will be used throughout the project for QC samples generated during sampling activities: • "QCEB" for Equipment Blanks • "QCFB" for Field Blanks (Note: GeoTracker needs to be prepopulated with Field Point Names to facilitate upload of well location GEO XY and analytical data.)
Field Organization (LOGCODE)	The following code will be used to identify the organization conducting field sampling activities: "TTSM" (for Tetra Tech, Inc., Santa Maria, CA)
Laboratory (LABCODE)	The following code will be used to identify the certified laboratory conducting analyses for the project: FGLE. FGLE notes samples will be sent to Fruit Growers Laboratory in Santa Paula, CA.
Project Name (PROJNAME)	The following code will be used to identify the project related to the data being uploaded: "CC Domestic Well Project"
Sample ID (SAMPID) Note: must be limited to 25 characters.	Same as Field Point Name (FIELD_PT_NAME) with the following added convention for QC duplicate samples prepared in the field (i.e., field duplicate) and submitted to the laboratory for analyses under COC: • for Field Duplicates, "DUP" will be added to the end of the Field Point Name (e.g., CCDW4DUP or CCDW4W2DUP)
Field Point Description (FIELD_PT_DESC)	One of the following codes will be used to identify where the sample was collected: •"Well Head" (for samples collected directly from well or well head) •"Distribution System" (for samples collected in the distribution system before any treatment devices)
Field Point Class (FIELD_PT_CLASS)	One of the following codes will be used to identify the system that was sampled: •"PRIW" (Domestic/Private Drinking Water Well) •"LSMWS" (Local Small Water System) •"SSMWS" (State Small Water System)
Well Screen Depth (SCREE_DEPTH)	Optional, enter data per EDF EDD standards if available.
Well Screen Length (SCREEN_LENGTH)	Optional, enter data per EDF EDD standards if available.
Well Location Coordinates (Latitude) (Longitude)	Enter the well location data via a GEO_XY file for each sampled well point, consisting of latitude and longitude (i.e., X,Y) coordinates measured in decimal degrees, and reported to 7 decimal points, with minimum accuracy of < 10 meters (1000 cm) with respect to North American Datum 1983 (NAD83) as measured by a global positioning system (GPS) device.

Table 4 (Continued)
GeoTracker GAMA Electronic Deliverable Format Fields

Data Field	Description
Survey Method (XY_METHOD)	Use one of the following survey methods per the EDF EDD standard guidelines: •"RTK" •"STAT" •"GNOR"
Survey Datum (XY_DATUM)	The following code will be used to identify the survey datum associated with the well location coordinates: "NAD83"
Survey Accuracy (XY_ACC_VAL)	Enter as appropriate per EDF EDD standard guidelines.
Surveying Organization/Entity (XY_SURVEY_ORG)	The following code will be used to identify the organization collecting well location coordinates: "TTSM" (for Tetra Tech, Santa Maria, CA)
Survey Equipment (GPS_EQUP_TYPE)	Select GPS equipment type from the valid value list presented in the EDF EDD standard guidelines. If appropriate equipment type does not exist on list, request new valid value from the SWRCB.
Electronic Report (GEO_REPORT)	This EDD file will be used to upload a single pdf document including the COC form(s) and associated Field Sampling Forms, photographs, etc., organized in order of relative sampling occurrence, for all wells sampled during each daily sampling event (i.e., one file per daily sampling event and associated COC transmittals). GEO_REPORT files will be named using the following convention (date represents the field sampling date): mm/dd/year COC & Field Sampling Documents Note: Field Sampling Forms contain confidential participant names, addresses and contact information (also see Section 18.1). To protect this information the GeoTracker project and associated GEO_REPORT electronic files will not be accessible on the public side of GeoTracker (i.e., the box on the GeoTracker Project Information page to make the project public will not be checked). However, the sampling results and well locations will be made available on the public side of GeoTracker GAMA by checking the "GAMA" box on the Project Information page.
Other Fields	Remaining required data fields associated with required EDD files shall be populated per EDF EDD standard guidelines.

Table 4, Page 2 of 2

6.8 PROJECT PARTICIPANT DATA TRANSMITTAL

Within five business days of completing the analyses and QA data review, FGL will transmit a data results and supporting information package (laboratory package) to the project participant consisting of the following:

- Standard cover/transmittal letter with CCRWQCB Project Manager contact information (Julia Dyer, (805) 542-4624, julia.dyer @waterboards.ca.gov), laboratory contact information, and a list of attachments;
- Analytical results report;

FGL will notify the Tetra Tech Project Manager when laboratory packages are sent to the project participants so the PPTDB can be updated. FGL will transmit laboratory packages to the participants by email, sent with a delivery receipt. Data packages will be sent by US Mail if FGL receives an "undeliverable" email response message, or no email address was provided during the intake process. Transmitted results will be considered delivered and tracked accordingly in the PPTDB unless they are

returned as undelivered to FGL by the internet service provider and/or postal service. FGL will inform Tetra Tech of any transmitted results that are returned as undelivered. Tetra Tech will attempt to contact the project participant and determine how best to proceed (e.g., email, send results to alternate address, etc.).

An example of the laboratory report and supporting information package documents are provided in Appendix C.

7.0 QUALITY OBJECTIVES AND CRITERIA

Consistency in the collection and analysis of project data is achieved through the application of universal measurement quality objectives (MQOs). As defined by the U.S. Environmental Protection Agency (EPA), these are acceptance criteria for data quality attributes such as precision, accuracy, sensitivity, and completeness. Adherence to the field and laboratory MQOs in this QAPP ensures that data generated by the project will be of known and documented quality.

7.1 FIELD SAMPLE QUALITY OBJECTIVES

The MQOs for measurements taken in the field using various meters and probes are summarized in Table 5.

Table 5
Measurement Quality Objectives for Field Measurements

Parameter	Probe/Meter	Units	Resolution	Reporting Limit	Accuracy
Depth	Electronic Depth Sounder	Feet	0.01	0.02	n/a
Dissolved Oxygen	Polarographic or Luminescence Quenching	mg/L	0.1	n/a	±0.2
pH	Electrode	None	0.1	n/a	±0.2
Specific Conductivity	Conductivity Cell	µS/cm	0.5	2	2
Temperature	Thermistor or Bulb	˚C	0.1 or 0.5	n/a	±0.1

Notes: ˚C degrees Celsius
µS/cm micro Siemens per centimeter
mg/L milligrams per liter
n/a not applicable

Quality control samples to be prepared in the field will consist of field blanks, field duplicates, and equipment blanks. These samples will be used to assess data quality relative to MQOs. Table 6 summarizes the field quality control samples and associated MQOs for this project.

Table 6
Field Quality Control Samples and Associated Measurement Quality Objectives

Quality Control Sample	Frequency of Analysis	Measurement Quality Objective
Field Duplicate	5% of total project sample count	RPD<25% (n/a if native concentration of either sample<RL)
Field Blank	5% of total project sample count	<RL for target analyte
Equipment Blank	5% of total project sample count	<RL for target analyte

Notes: n/a not applicable
RL reporting limit
RPD relative percent difference

Table 7 provides a list of QA codes – to be noted within the electronic data files uploaded to GeoTracker GAMA – if field quality control samples fail the associated MQO.

Table 7
Field Quality Assurance Codes

QA Sample Type	QA Issue	Quality Code
Field blank	Analyte detected in field blank above the RL	VFB
Field blank	Analyte detected in field blank and >1/5 amount detected in field sample	FI
Field duplicate	RPD is >25%	VFD
Equipment blank	Analyte detected in equipment blank and >1/5 amount detected in field sample	IP

Notes: RPD relative percent difference

7.1.1 Field Blanks

Field blanks will be prepared in the field and exposed to the same conditions as the sample. Its purpose is to assess the potential for field contamination. Field blanks will be prepared and analyzed for all analytes of interest at the rate of 5% of total project sample count, and will be collected along with the associated environmental samples

Field blanks will be prepared by pouring laboratory-grade water into applicable sample collection containers, labeled and stored according to the procedures for samples collected at the well. If any analytes of interest are detected at levels greater than the Reporting Limit (RL) for the parameter, the sampling crew should be notified so that the source of contamination can be identified, the results qualified according to Table 7, and corrective measures taken prior to the next monitoring event. If the analyte concentration in the blank is greater than 1/5 the concentration of the associated field sample, the results for the environmental samples may be unacceptably affected by contamination and should be qualified in the electronic data deliverables as noted in Table 7. If contamination is detected, field blanks must be collected at a rate of 10% of samples until the next audit.

7.1.2 Field Duplicates

The purpose of analyzing field duplicates is to demonstrate the precision of field sampling techniques as well as accounting for environmental variability and precision of the laboratory analysis. Field duplicates will consist of two grab samples, collected in rapid succession, for all laboratory constituents. Field

duplicates will be collected at the rate of 5% of total project sample count, and analyzed along with the associated environmental samples. Field duplicates will be used to evaluate the Relative Percent Difference (RPD) between regularly collected field samples and the corresponding duplicate samples. The measured value for each field sample will be compared to the measured value for the corresponding field duplicate, and the RPD will be expressed as:

$$RPD = \frac{Vm - Vk}{0.5(Vm + Vk)} \times 100\%$$

where: RPD = the relative percent difference
Vm = the measured value in the duplicate sample
Vk = the measured value of the primary field sample

If the RPD of the field duplicate is greater than 25% and the absolute difference is greater than the RL, both samples should be reanalyzed. If an RPD greater than 25% is confirmed by reanalysis, environmental results will be qualified as estimated. High RPD results will be designated in electronic data deliverables as noted in Table 7. The sampling crew should also be notified immediately so that the source of sampling variability can be identified (if possible) and corrective measures taken prior to the next monitoring event.

7.1.3 Equipment Blanks

Improper sampling equipment decontamination could lead to sample cross-contamination. Therefore, equipment blanks, also known as rinsate blanks, will be collected in order to assess the adequacy of the sampling equipment decontamination process. Equipment blanks will be prepared and analyzed for all analytes of interest at the rate of 5% of total project sample count, and will be collected along with the associated environmental samples. As with the field blank, if any analytes of interest are detected at levels greater than the RL for the parameter, the sampling crew should be notified so that the source of contamination can be identified, results qualified according to Table 7, and corrective measures taken prior to the next monitoring event. If the analyte concentration in the equipment blank is greater than 1/5 the concentration detected in the associated well sample(s), the results for the associated sample(s) may be unacceptably affected by contamination and should be qualified in the electronic data deliverables as noted in Table 7.

7.2 LABORATORY QUALITY OBJECTIVES

Quality control samples prepared by FGL will typically consist of method blanks, certified reference materials, laboratory duplicates, matrix spikes, and matrix spike duplicates. Continuing calibration verification and spikes (laboratory control sample, matrix spike, and matrix spike duplicate) cannot be performed on total dissolved solid and alkalinity samples. Table 8 summarizes the laboratory quality control samples and associated MQOs for this project.

Table 8
Laboratory Quality Control Samples and Associated Measurement Quality Objectives

Quality Control Sample	Frequency of Analysis	Measurement Quality Objective
Calibration Standard	Per analytical method or manufacturer's specification	Per analytical method or manufacturer's specification
Continuing Calibration Verification	Per 10 analytical runs	80-120% recovery
Method Blank	Per 20 samples or per analytical batch whichever is more frequent	<RL for target analyte
Laboratory Control Sample	Per 20 samples or per analytical batch, whichever is more frequent	80-120% recovery
Matrix spike	Per 20 samples or per analytical batch, whichever is more frequent	80-120% recovery
Matrix spike duplicate	Per 20 samples or per analytical batch, whichever is more frequent	80-120% recovery RPD, 25% for duplicates
Laboratory Duplicate	Per 20 samples or per analytical batch, whichever is more frequent	RPD<25% (n/a if native concentration of either sample <RL)
Internal Standard	Accompanying every analytical run as method appropriate	Per method

Notes: n/a not applicable
RL reporting limit
RPD relative percent difference

Table 9 provides a list of QA codes – to be noted within the electronic data files uploaded to GeoTracker GAMA if field quality control samples fail the associated MQO.

Table 9
Laboratory Quality Assurance Codes

QA Sample Type	QA Issue	QA Code
Method blank	Analyte detected in blank and > reporting limit	B
Method blank	Analyte detected in blank and > 1/5 amount detected in field sample	VQB
Laboratory Control Sample	Percent recovery exceeds control limit	TW
Laboratory Duplicate	relative percent difference is >25 percent	IL
Matrix Spike	Percent recovery outside control limit	GB
Matrix Spike Duplicate	relative percent difference is >25%	IL

Note: MDL Method Detection Limit

7.2.1 Method Blanks

The purpose of analyzing method blanks is to demonstrate the analytical procedures do not result in sample contamination. Method blanks will be prepared and analyzed by FGL at a rate of at least one for each analytical batch. Method blanks will consist of laboratory-prepared blank water processed with the batch of environmental samples. The method blank should be prepared and analyzed before analysis of the associated environmental samples. If the result for a single method blank is greater than the RL, or the analyte is detected in the blank and greater than 1/5 amount detected in the filed sample, the source(s) of contamination should be corrected and the associated samples should then be

reanalyzed. If reanalysis is not possible, the associated sample will be designated in the EDF as noted in Table 9.

7.2.2 Laboratory Control Samples

The purpose of analyzing laboratory control samples (i.e., laboratory-fortified method blanks) is to demonstrate the accuracy and precision of the analytical methods. Laboratory control samples will generally be analyzed at the rate of one (of each type of control sample) per sample batch. Recovery is the accuracy of an analytical test measured against a known analyte addition to a sample. Percent recovery is calculated as follows:

$$R = \frac{Mc}{Sc} \times 100$$

where: R = Recovery as a percentage of the total spiked concentration
Mc = the measured concentration
Sc = the spiked concentration

If recovery of any analyte is outside the acceptable range for accuracy (i.e. 80% to 120% recovery), the analytical process is not being performed adequately for that analyte. In this case, the sample batch should be prepared again, and the laboratory control sample should be reanalyzed. Bias is the systematic or persistent distortion of a measurement process that causes errors in one direction. If reanalysis is not possible, the associated sample results will be designated in electronic data deliverables as noted in Table 9.

7.2.3 Laboratory Duplicates

The purpose of analyzing laboratory duplicates is to demonstrate the precision of the analytical method. Laboratory duplicates will be analyzed at the rate of one pair per sample batch, or one in 20 samples, whichever is more frequent. Laboratory duplicates will consist of duplicates of sample waters from FGL. If the RPD for any analyte is greater than the precision criterion (25% for conventional constituents) *and* the absolute difference between duplicates is greater than the RL, the analytical process is not being performed adequately for that analyte. In this case, the sample batch should be prepared again, and laboratory duplicates should be reanalyzed. If reanalysis is not possible, the associated sample results will be designated in electronic data deliverables as noted in Table 9.

7.2.4 Matrix Spikes and Matrix Spike Duplicates

The purpose of analyzing matrix spikes and matrix spike duplicates is to demonstrate the accuracy (matrix spike) and precision (matrix spike duplicate) of the analytical method in a particular sample matrix. Matrix spikes and matrix spike duplicates will be analyzed at the rate of one pair per sample batch, or one in 20 samples, whichever is more frequent. Each matrix spike and matrix spike duplicate will consist of an aliquot of laboratory-fortified environmental sample. Set spike concentration levels will be employed using a premixed standard containing all constituents at the same concentration. QC reports will include the actual spike concentrations on the final report. Recovery is the accuracy of an analytical test measured against a known analyte addition to a sample. Percent recovery is calculated as follows:

$$R = \frac{(Matrix\ plus\ spike\ result - Matrix\ result)}{Expected\ matrix\ plus\ spike\ result} \times 100$$

If matrix spike recovery of any analyte is outside the acceptable range (i.e. 80% to 120% recovery), the results for that analyte will be determined not to meet the acceptance criteria. If recovery of laboratory control samples (i.e. those using blank water rather than sample matrix) is acceptable, the analytical process is being performed adequately for that analyte, and the problem is attributable to the sample matrix. An attempt should be made to correct the problem (by dilution, concentration, etc.), followed by re-analysis of the samples and the matrix spikes. If the matrix problem cannot be corrected, the results will be designated in electronic data deliverables as noted in Table 9.

If the matrix spike duplicate RPD for any analyte is greater than the precision criterion (25%), the results for that analyte will be determined not to meet the acceptance criteria. If the RPD for laboratory duplicates (i.e., those using blank water rather than sample matrix) is acceptable, the analytical process is being performed adequately for that analyte, and the problem is attributable to the sample matrix. An attempt should be made to correct the problem (by dilution, concentration, etc.), followed by re-analysis of the samples and the matrix spike duplicates. If the matrix problem can't be corrected, the results for that analyte will be designated in electronic data deliverables as noted in Table 9.

8.0 SPECIAL TRAINING/CERTIFICATION

Sampling Technicians will receive training to ensure that the work is conducted correctly and safely. At a minimum, all Sampling Technicians will have experience with the sampling guidelines specified in Section 6.0 of this QAPP. Sampling Technicians are required to read the QAPP prior to going to the field and to have a copy of the QAPP with them while sampling. A copy of training records will be maintained for all Sampling Technicians.

FGL must be certified according to the State Water Resources Control Board Environmental Laboratory Accreditation Program (ELAP). FGL staff must have demonstrated experience with each method and familiarity with the laboratory standard operating procedures (SOP). FGL is required to comply with the procedures documented in this QAPP.

All work shall be performed under the supervision of the Project Manager experienced with the sampling guidelines specified in Section 6.0.

9.0 DOCUMENTS AND RECORDS

9.1 QAPP AMENDMENTS

Refer to Section 4.3 of this QAPP for information regarding the process and responsibilities of ensuring that the appropriate project personnel have the most current approved version of the QAPP.

9.2 PROJECT PARTICIPANT AND TRACKING DATABASE

The Tetra Tech Project Manager and Sampling Coordinators will manage the *Project Participant and Tracking Database* (PPTDB; Appendix A). This database will reside on Tetra Tech's network of servers and will remain secure. This database will only be made available to the CCRWQCB and Tetra Tech staff and will be labeled and maintained as "Confidential" to protect participant and well location information. As noted in section 6 of this document, the database will be utilized to track all aspects of this project; from important project participant information collected during the intake process, to tracking submittal and delivery of the sample results to the participants.

9.3 SAMPLING AND REPORTING DOCUMENTATION

9.3.1 Central Coast Domestic Well Sampling Field Sampling Form

The *Central Coast Domestic Well Sampling Field Sampling Form* (Field Sampling Form; Appendix B) will be used for each well sampled to document site information, well stabilization data, and sample collection information. Hard copies of the Field Sampling Form will be retained by Tetra Tech for future use if needed. All Field Sampling Forms will be label and maintained "Confidential" to protect participant and well location information.

9.3.2 Chain-Of-Custody Form

A COC form (Appendix D) will accompany the samples at all times. The COC form will be consistent with the sample label, and will indicate the analyses to be performed, number of containers, sample volume, preservatives and container type for each sample. Completed COC forms will be retained by Tetra Tech for future use if needed.

SECTION B – DATA GENERATION AND ACQUISITION

10.0 SAMPLING PROCESS DESIGN

The Central Coast Domestic Well Sampling Project has a judgment-based sampling design that has an unknown number of monitoring sites across the Central Coast Region (Figure 3). The frequency of monitoring is dependent upon the desire of project participants to have their well(s) sampled. As allowed by the project participant, sampling will be performed within one month of a project participant requesting support.

All information collected under this QAPP will be reported to the CCRWQCB, including field observations and notes recorded during sample collection. Data that do not meet the QA/QC criteria in this document, or that do not meet the completeness standard may still be used. However, data not meeting QAPP requirements must be flagged and reported appropriately.

11.0 SAMPLING METHODS

Groundwater samples will be collected for conventional water quality characteristics following the guidelines in Section 6.4 of this QAPP. For each method described, it is the responsibility of the Sampling Technicians to determine whether the performance requirements of the sampling method have been met, and to collect an additional sample if required.

All water quality samples will be collected using techniques that minimize sample contamination, and sampling equipment will be decontaminated using Alconox and deionized water. Groundwater will be collected directly into the primary sample container. Sample containers will be appropriate for the analyses specified in this document (see Table 10 for bottle requirements).

Table 10
Sample Container, Preservative, and Holding Time Requirements

Parameter(s)	Sample Container	Sample Volume	Preservatives	Holding Time*
Total Dissolved Solids	Polyethylene	1 quart	None	7 days
Alkalinity as $CaCO_3$				14 days
Sulfate				28 days
Chloride				28 days
Nitrate as N	Polyethylene	1/2 pint	None	48 hours
Calcium	Polyethylene	250 mL	HNO_3; Store at 0-6°C	6 months
Magnesium				6 months
Sodium				6 months
Potassium				6 months
Arsenic				6 months
1,2,3-Trichloropropane	Glass	4X40 mL VOAs	$Na_2S_2O_3$	14 days
Chromium VI**	Polyethylene	1/2 pint	Preservative Buffer	14 days
Perchlorate	Polyethylene	1 pint	None	28 days

Notes:
* Holding times for all analytes default to the shortest analyte holding time for the sampling event: 48 hours
** pH must be verified in the field by sampling staff prior to shipment (no more than 24 hours after collection). If pH falls outside the acceptable range, a dilute acid or base must be added to stabilize the pH; after which holding time becomes 5 days
°C degrees Celsius
$CaCO_3$ calcium carbonate
H_2SO_4 sulfuric acid
HNO_3 nitric acid
mL milliliter
N nitrogen

$Na_2S_2O_3$	sodium thiosulfate
VOA	volatile organic analysis

If the performance requirements for specific samples are not met, the sample will be re-collected. If contamination of the sample container is suspected, a fresh sample container will be used.

Sampling Technicians will carry copies of the QAPP with them in the field for reference during sampling. Descriptions of specific sampling methods and requirements are summarized in Section 6.0. When problems occur in the field, the Tetra Tech Project Manager and/or QA Manager will assist the Sampling Technicians with resolving the issue; the QA Officer will be the final arbiter for any unresolved issues.

11.1 SAMPLE IDENTIFICATION SCHEME

Refer to Table 4, GeoTracker GAMA Electronic Deliverable Format Fields, for information related to sample identification.

11.2 FIELD MEASUREMENTS

Field parameters consisting of pH, specific conductance, and dissolved oxygen will be measured and documented in the field on the Field Sampling Forms. Field measurements will be made using a YSI field meter. Alternative field meters that meet the specified reporting limits may also be used. Measurements must be recorded on the Field Sampling Form prior to departing each well. Field meters must be calibrated before and after each day of sampling. During a multi-day event, the "post-sampling" calibration for the first day may serve as the "pre-sampling" calibration for the second day, and so on.

12.0 SAMPLE HANDLING AND CUSTODY

This section describes the requirements for sample handling and custody in the field, laboratory and transport.

12.1 FIELD SAMPLE HANDLING AND CUSTODY

Field personnel have the following responsibilities:

- Keeping an accurate written record of sample collection activities using the Field Sampling Form;
- Ensuring that all entries are legible, written in waterproof ink and contain accurate and inclusive documentation of the field activities;
- Noting errors or changes using a single line to cross out the entry and date and initial the change;
- Completing the COC forms accurately and legibly;
- Affixing a label to each sample collected. Sample labels uniquely identify samples with an identification number, date and time of sample collection and the initials of the sampling crew;
- Sealing ice chests with tape and a custody seal before shipping; and

- Ensuring samples are delivered to the laboratory by 3:00 PM on the day of sampling or no more than 32 hours after collection. This will require communicating with FGL for courier availably or identifying FedEx locations to drop samples off for next-day priority delivery.

In the field, all samples will be packed in wet ice during shipment, to maintain sample temperatures at 0-6˚C until analyzed. Prior to shipping, all sample caps and lids will be checked for tightness, and placed in the ice chest with enough ice (in Ziploc bags or tied-off trash bags) to completely fill the ice chest. Samples will be shipped in insulated containers either via same-day courier or via overnight freight.

A COC form will be completed after sample collection, and confirmed for accuracy prior to sample shipment or release. Specifically, the COC form, sample labels, and field documentation will be crossed-checked to verify sample identification (Field Point Name), type of analyses to be performed, number of containers, sample volume, preservatives and container type. Information to be included on the COC forms includes:

- Name and address of the receiving laboratory (FGL);
- Contact information for responsible party within the Central Coast Domestic Well Sampling Program;
- Sample identification (Field Point Name);
- Date and time of collection;
- Sampler(s) names;
- Analytical method(s) requested;
- Sample matrix;
- Signature blocks with date and time for release and acceptance of samples; and
- Any comments to identify special conditions or requests.

Sample transfer between field staff and laboratory is documented by signing and dating "relinquished by" and "received by" blocks located on the COC form whenever sample possession changes. If samples are not shipped on the collection day, they will be refrigerated in a sample control area with temperature of 0-6°C. An example COC form is included as Appendix D.

All sample shipments will be accompanied by the COC form that identifies the contents of the cooler; the original form accompanies the shipment and a copy is retained by the field crew and submitted to the Tetra Tech Project Manager and QA Manager upon completion of sampling. COC forms will be placed in a plastic Ziploc bag and taped to the inside of the ice chest lid.

Ice chests will be sealed with tape and a custody seal before shipping. All water quality samples will be transported to FGL directly by the Sampling Technician(s) or by overnight courier. Due to the 48-hour holding time for nitrate (as N), samples must be delivered to the Satellite Laboratory by 3:00 PM and no more than 32 hours after collection to the Santa Paula Laboratory. Samples are shipped to FGL according to Department of Transportation standard.

12.2 LABORATORY CUSTODY

FGL will have a sample custodian who will examine the samples for correct documentation, proper preservation and holding times, and will follow sample custody procedures outlined in the laboratory QAPP. The FGL QAPP is included as Appendix E. The following sample control activities must be conducted by FGL:

- Initial log-in and verification of samples received with the COC form;
- Documentation of any discrepancies on the COC form;
- Verify and inspect sample preservation methods such as temperature and/or chemical preservative;
- Notify the Tetra Tech Project Manager if any problems or discrepancies are identified;
- Ensure proper sample storage, including daily monitoring of storage temperature and sample security;
- Ensure timely extraction or additional preservation steps based on hold times identified for the analytical method to be performed;
- Distribute samples or notify the laboratory of sample arrival;
- Sealed ice chests dropped off at the FGL satellite lab will not be opened to verify contents prior to shipping to the Santa Paula laboratory; and
- Return coolers to Sampling Technicians.

FGL shall maintain custody logs sufficient to track each sample submitted and to verify that samples are preserved, extracted and analyzed within specified holding times. The COC form, any shipping documents, completed cooler receipt forms, telephone conversation record forms, and any corrective action forms will be maintained by FGL for each shipment and included in the reporting package when the results are submitted.

13.0 ANALYTICAL METHODS

A summary of analytical methods for parameters measured in the field and laboratory are presented in Table 11. Grab samples will be analyzed by FGL according to the methods specified in Table 11 and pursuant to FGLs Standard Operating Procedures, which are included as Appendix F.

Table 11
Analytical Methods and Reporting Limits for Field and Laboratory Parameters

Parameter	Method	RL	MDL	Holding Time
pH	Field/SM 4500-H+B	NA	NA	NA
Specific Conductance	Field/SM 2510B	1 µS/cm	NA	NA
Dissolved Oxygen (w/ optical probe)	Field/ASTM Method D888-09 (C)	0 mg/L	NA	NA

Parameter	Method	RL	MDL	Holding Time
Dissolved Oxygen (w/ membrane probe)	Field/SM 4500-O-G-2001	0 mg/L	NA	NA
Total Dissolved Solids	FGL/SM 2540C	10 mg/L	5.8 mg/L	7 Days
Total Alkalinity as $CaCO_3$	FGL/SM 2320B	10 mg/L*	1.1 mg/L	14 Days
Calcium	FGL/EPA 200.7	0.5 mg/L	0.015 mg/L	6 Months
Magnesium	FGL/EPA 200.7	0.5 mg/L	0.012 mg/L	6 Months
Sodium	FGL/EPA 200.7	0.5 mg/L	0.014 mg/L	6 Months
Potassium	FGL/EPA 200.7	0.1 mg/L	0.082 mg/L	6 Months
Sulfate	FGL/EPA 300.0	1 mg/L	0.092 mg/L	28 Days
Chloride	FGL/EPA 300.0	1 mg/L	0.063 mg/L	28 Days
Nitrate (as N)	FGL/EPA 300.0	0.1 mg/L	0.007 mg/L	48 Hours
Arsenic	FGL/EPA 200.8	0.5 µg/L	0.011 µg/L	6 Months
1,2,3-Trichloropropane	FGL/SRL 524-TCP	0.005 µg/L	0.0019 µg/L	14 Days
Chromium VI	FGL/EPA 218.6	0.1 µg/L	0.012 µg/L	14 Days
Perchlorate	FGL/EPA 314.0	2 µg/L	0.29 µg/L	28 Days

Notes:

ASTM	American Society for Testing and Materials
$CaCO_3$	calcium carbonate
EPA	Environmental Protection Agency
FGL	Fruit Growers Laboratory
MDL	method detection limit
µg/L	micrograms per liter
µS/cm	micro Siemens per centimeter
mg/L	milligrams per liter
RL	reporting limit
SM	Standard Method
*	if result is <10 mg/L, sample will be re-analyzed by manual titration using 200 mL sample volume instead of 50 mL to achieve RL of 2 mg/L

Data quality will be attained by maximizing and documenting the accuracy and precision of the analytical methods used. Any changes in procedures due to equipment changes or to improved precision and accuracy will be documented.

13.1 VALIDATION OF ANY NON-STANDARD METHODS

For non-standard sampling and analysis methods, sample matrices, or other unusual situations, appropriate method validation study information shall be documented to confirm the performance of the method for the particular need. The purpose of this validation method is to assess potential impact on the representativeness of the data generated. If previous validation studies are not available, some level of single-user validation study should be performed during the project and documented. Approval of non-standard methods ultimately is the responsibility of the Central Coast Water Board QA Officer.

13.2 DETECTION AND QUANTITATION LIMITS

The MDL and quantitation limits (QLs) must be distinguished for proper understanding and data use. The MDL is the minimum analyte concentration that can be measured and reported with a 99% confidence that the concentration is greater than zero. The QL represents the concentration of an analyte that can be routinely measured in the sampled matrix within stated limits and confidence in both identification and quantitation. For this project, QLs must be verifiable by having the lowest non-zero calibration standard or calibration check sample concentration at or less than the QL.

For this program, QLs have been established based on the verifiable levels and general measurement capabilities demonstrated for each method to meet the MQOs. Note that samples diluted for analysis may have sample-specific QLs that exceed the anticipated method QLs. This will be unavoidable in some cases.

The QLs that will be reported by FGL for this project will be referred to as "Reporting Limits" (RLs). The RLs used by FGL will be less than or equal to the RLs specified in this QAPP and FGL will have documentation to support quantitation at those levels.

FGL will report analytical results that fall between the MDL and project RL. These results will be reported as the numeric measured values and qualified as estimates. Reporting as "trace" or "<RL" is not acceptable. The Tetra Tech QA Manager will assess this information's usability. Analytical results that fall below the MDL will be reported as "not detected."

13.3 CORRECTIVE ACTIONS

The Tetra Tech QA Manager will review field data for compliance with this QAPP, whereas FGL's QA Director will be responsible for maintaining compliance with the QC requirements described later in this QAPP. The Tetra Tech QA Manager will notify the Tetra Tech Project Manager of any violation of QC protocol by the field crews, and will generate a corrective action and document future compliance. As required by their ELAP certification, FGL's QA Director will generate corrective actions for violations of QC protocols. The FGL QA Director will also notify the Tetra Tech Project Manager and QA Manager of deviations from QC protocols that are related to samples collected for this project.

13.4 SAMPLE DISPOSAL

All samples remaining after successful completion of analyses will be disposed of properly. It is the responsibility of FGL personnel to ensure that all applicable regulations are followed in the disposal of samples or related chemicals. FGL's QA Director must approve the disposal of any sample.

13.5 LABORATORY TURNAROUND TIME

Analytical testing will be performed by FGL using standard turnaround-times of 12-15 business days from receipt of samples. Water quality results will be provided to project participants within five business days of completing the sample analysis and QA data review.

14.0 QUALITY CONTROL

There is potential for variability in any sample collection, analysis, or measurement activity. Field variability generally contributes more than laboratory variability. Quality control sample requirements (e.g., field blanks and field duplicates/splits) and schedules are summarized in Tables 4 through 8.

Should contamination be detected in field blank samples, the Tetra Tech QA Manager will contact the FGL and seek additional laboratory QC analyses (e.g., lab blank water analysis, bottle analyses). In addition, the Tetra Tech QA Manager will review notes recorded in the field log to determine if a possible source of contamination is identified in the notes. Should this additional data prove to not identify the source of the contamination, the following additional analyses may be added to a future event: bottle blank, trip blank, and equipment blank. If the field sampling is determined to be the source of the contamination, following the collection of these additional QC samples, the Tetra Tech QA Manager may implement additional training to ensure that the issue does not re-occur.

Comparability of the data can be defined as the similarity of data generated by different monitoring programs. For the purpose of this project, this objective is addressed primarily by using standard sampling and analytical procedures, and regionally relevant measurement quality objectives, where possible. Additionally, comparability of analytical data is addressed by analysis of certified reference materials (discussed previously in Section 7.0).

Representativeness can be defined as the degree to which the environmental data generated by the monitoring program accurately and precisely represent actual environmental conditions. For this project, this objective is addressed by the overall design of the monitoring program. For example, properly purging and stabilizing the well, selecting appropriate methods for each environmental parameter, and by maintaining the integrity of the sample after collection. Each of these quality control elements are addressed elsewhere in this document.

15.0 INSTRUMENT/EQUIPMENT TESTING, INSPECTION, CALIBRATION, AND MAINTENANCE

15.1 FIELD EQUIPMENT

Well sampling will be achieved using a YSI field meter, which must be properly calibrated each morning before sampling activities, and at the end of each sampling day. Each instrument to be used in the field will be calibrated within a range expected to bracket results from well sampling. If a result in the field lies outside of the calibration limits, the instrument will have to be calibrated again with standards that bracket the result. Calibration methods are as follows:

1. pH is calibrated using a three-point method of 4.1, 7.0, and 10.1 solutions.
    - The sensor is rinsed in the solution being used for calibration prior to readings.
    - Readings off by greater than 0.3 are deemed failing.
2. Specific conductivity is calibrated using standard solution of 1,000 µS/cm.
    - Post-calibration readings are not to be off by more than ± 5%.
3. DO (percent-saturation) is calibrated by comparing barometric pressure, temperature and the fully water-saturated DO readings against theoretical DO values.
    - Post-calibration readings are not to be off by more than ± 0.5 mg/L, ± 6% saturation.
4. After calibration, the sensor is rinsed and stored in a neutral pH solution.

Should the calibration result in errors that do not meet the instrument's specifications, the Sampling Technician must recalibrate the instrument. Should errors still occur, a calibration should be performed with new calibration solutions and/or maintenance should be performed (e.g., replace DO membrane, check batteries, etc.). If field calibration with new standards reveals that the instrument is outside established accuracy limits, the instrument may be serviced in the field with the service kit provided by the manufacturer. Sampling Technicians will carry the necessary equipment manuals and repair kits to provide basic repair services for the equipment should a failure include in the field; however, Sampling Technicians may use their judgment to determine whether it is preferable to perform in-field servicing or turn to a back-

up instrument. Backup instruments should be available for each of the critical real-time instruments used in the field (e.g., field meters, smartphone or disposable camera, thermometer, etc.). In the event that a field instrument cannot be properly calibrated and the in-field servicing does not mitigate the calibration problems, then the back-up instrument should be used. If the backup instrument also fails, grab samples may be collected and sent to a laboratory for analysis to maintain data set completeness. If the errors in the calibration cannot be rectified, the Sampling Technician must report the problem to the Tetra Tech Project Manager and QA Manager and record the appropriate information on the calibration sheets. The meter should immediately be returned to the manufacturer for maintenance and an identical loaner meter should be requested. All calibration data must be recorded.

The YSI probe used for the collection of pH and conductivity analysis will require routine maintenance and cleaning to ensure accurate results in the field. It is the responsibility of the Sampling Technician to ensure that all maintenance is done. This includes properly cleaning and storing the instrument as well as checking the probes and cables for any issues. Sampling Technicians must carry sufficient calibration/cleaning solutions as well as spare parts to accomplish sampling tasks.

For recording well location, a Trimble GeoXH GPS or comparable device capable of achieving sub meter accuracy will be used. In order to ensure accurate results, a minimum number of satellite connections are required to collect a point. The Trimble GeoXH or comparable device data collection settings will be reviewed prior to field use to ensure only sub meter accurate points are collected. Data will be collected with respect to the North American Datum of 1983 (NAD 83). At the end of each day, GPS points will be downloaded from the GPS unit and copied over to the PPTDB.

Depth-to-water and well depth will be recorded using an electronic water sounder capable of reading to 0.01-inches. The sounder is "bench calibrated" by the manufacturer and will not require further calibration unless Sampling Technicians suspect faulty readings. If faulty readings are suspected, the sounder will be sent back to the manufacturer for maintenance. After each use, the sounder measuring tape shall be cleaned using a weak bleach solution of one parts household bleach to four parts water (i.e., 1:4 ratio). The sounder measuring tape will be cleaned using the weak bleach solution as it is retracted from the well. It is imperative a clean sounder is used at each well to avoid cross-contamination.

Appendix G contains an example copy of the calibration form used for all instruments associated with this project requiring routine calibrations. In the event of malfunctioning measurement devices, a backup device will be on hand for emergencies. If both devices are not working properly, all sampling activities that do not require the malfunctioning instruments will be performed, and sampling completed. At the end of each day, all instruments will be thoroughly cleaned to remove any residue and properly stored until the next sampling event occurs.

15.2 LABORATORY EQUIPMENT

FGL's analytical equipment will be calibrated and maintained using the frequency and procedures outlined in its Quality Assurance Manual. FGL must have sufficient spare parts for all testing equipment so as to meet holding time limits and other QC measures specified in this QAPP. Deficiencies in equipment calibration will be managed in accordance with FGL's Quality Assurance Manual. Equipment calibration issues that could affect the data quality for the project governed by this QAPP must be reported to the Tetra Tech QA Manager, and affected data flagged accordingly. Laboratory Quality Assurance Manuals must be made available for review at the analyzing laboratory if requested by the Tetra Tech QA Manager.

16.0 INSPECTION/ACCEPTANCE FOR SUPPLIES AND CONSUMABLES

The procurement of supplies, equipment, and services must be controlled to ensure that specifications are met for the high quality and reliability required for each field and laboratory function. All equipment and material specifications used by FGL or Tetra Tech Sampling Technicians for well sampling and analysis are outlined in this QAPP or the respective operating procedures and policies. Equipment and materials are purchased independently by FGL, or by Tetra Tech. It is the responsibility of each staff person doing the ordering to inspect the equipment and materials for quality. Upon receipt of materials or equipment, a designated employee receives and signs for the materials. The items are reviewed to ensure that the shipment is complete and they are then delivered to the proper storage location. All chemicals are dated upon receipt. All supplies are stored appropriately and are discarded upon expiration date.

17.0 DATA ACQUISITION REQUIREMENTS FOR NON-DIRECT MEASUREMENTS

At this time, non-direct measurements (e.g., computer databases, literature files, etc.) from sources other than a laboratory or field meter are not anticipated.

18.0 DATA MANAGEMENT

Various forms of information and data (i.e., field sampling forms, the PPTDB, COCs, laboratory reports, photographs, etc.) will be generated during this project from various project representatives (i.e., Sampling Coordinators, Sampling, Technicians, Laboratory Staff, Project Managers, etc.). It is important such information is easily assessable, safe, and organized should it need accessed in the future. Data related to this project will be aggregated by sampling event and uploaded to GeoTracker as described below.

A single pdf file containing the COC forms, field sampling forms and associated photographs generated during each daily sampling event (i.e., one file per sampling event and associated COC transmittals) will be uploaded to GeoTracker as a GEO_REPORT electronic file as described in Section 6.5 of this document. Electronic pdf copies of laboratory analytical reports provided to Tetra Tech by FGL for QA purposes as well as the final data reports will be retained by Tetra Tech for a minimum of 5-years from the date which the record was produced. Copies of the final data reports will be retained by FGL as well for a minimum of 5-years. A copy of the PPTDB and associated files (e.g., laboratory reports) will be provided to the Water Board at the end of the project, or upon request.

18.1 DATA CONFIDENTIALITY

All documents containing participant names, addresses and contact information will be labeled and maintained as confidential documents. In general, these include the PPTDB, Field Sampling Forms and laboratory analytical reports. To protect this information the GeoTracker project and associated GEO_REPORT electronic files will not be accessible on the public side of GeoTracker. This will be accomplished by not checking the box on the GeoTracker Project Information page to make the project public. However, the sampling results and well locations will be made available on the public side of GeoTracker GAMA by checking the "GAMA" box on the Project Information page.

SECTION C – ASSESSMENT AND OVERSIGHT

Assessments of compliance with quality control procedures will be undertaken for each monitoring event during the data collection phase of the project:

- Sampling Technicians will conduct a performance assessment of the sampling procedures each day of sampling. Corrective actions shall be carried out by the field sampling crew, recorded in the field log, and reported to the Program QA Officer.

- The project QA Manager will review the sampling forms and associated COC forms within 10 business days of sample collection and develop corrective actions should errors be observed. Periodic field audits will be conducted by the Central Coast Water Board.

- Assessment of laboratory QC results and implementation of corrective actions will be the responsibility of the FGL QA Director and will be reported to the project QA Manager as part of any data reports.

- The project QA Manager will review of the laboratory hard copy and electronic reports within 10 business days of receipt (or at ~30 business days post-collection) and develop corrective actions should errors be observed.

Routine procedures to assess precision and accuracy, criteria for success, and corrective actions have been discussed previously in this QAPP. During the course of sample collection and analysis, the laboratory supervisors and analysts, and field supervisors and team members will make sure that all measurements and procedures are followed as specified in this QAPP, and measurements meet the prescribed acceptance criteria. If a problem arises, prompt action to correct the immediate problem and to identify its root causes is imperative. Any related systematic problems must also be identified. Problems regarding analytical data quality that require corrective action are documented in FGL's guidance documents. Problems regarding field data quality that may require corrective action are documented in the sampling forms. The QA Manager is responsible for reviewing field data for QC compliance, whereas the FGL QA Director is responsible for maintaining compliance with the QC requirements described in the lab's QC manuals and policies. The Tetra Tech QA Manager will notify the Project Manager of any violation of QC protocol by the Sampling Technicians, and the QA Manager will generate a corrective action and document future compliance. As required by their ELAP accreditation, FGL's QA Director is responsible for generating corrective actions for violations of QC protocols, and must also notify the Tetra Tech QA Manager of deviations from QC protocols that are related to samples collected for this project. Corrective actions will be documented and included in the analytical data report for each sample.

The Tetra Tech QA Manager will maintain an open dialogue with FGL and Sampling Technicians regarding the QC review performed following each well sampling, and will maintain a QA Log of all communications and any specified corrective actions. The QA Manager will make the QA Log available to the Central Coast Water Board upon request. The QA Manager is authorized to submit stop work orders to the Project Manager should a laboratory or Sampling Technician prove incapable of meeting the project QA/QC requirements. The Project Manager must communicate the reasoning for the stop work order to the Central Coast Water Board.

19.0 REPORTS TO MANAGEMENT

The *Project Participant and Tracking Database* (PPTDB) will be submitted to the Central Coast Water Board Contract Manager along with project invoices. The frequency of these submittals will be dependent upon participation by well owners, or quarterly at a minimum. The Central Coast Water Board Contract Manager will crosscheck the PPTDB with the data and electronic reports uploaded to GeoTracker to validate the invoices. All original electronic laboratory reports (i.e., in a pdf format) will be retained by Tetra Tech and FGL as noted in Section 18 above and be provided to the Central Coast Water Board upon request. Any errors or formatting issues identified in the submitted data will be revised by Tetra Tech or FGL within five business days of identifying the error.

SECTION D – DATA VALIDATION AND USABILITY

20.0 DATA REVIEW, VERIFICATION, AND VALIDATION

Data generated by project activities will be reviewed against the data quality objectives cited in Section 7 of this QAPP. Once reviewed, data will fall into three categories: meeting all measurement requirements, failing precision or recovery criteria, or failing accuracy criteria. Data meeting all measurement quality objectives, but with failures of QA/QC practices will be set aside until the impact of the failure on data quality is determined. Once determined, the data will be moved into either the first category or the last category.

Data falling in the first category are considered usable by the project. Data falling in the last category are considered unusable. Data falling in the second category will be assessed for all QA/QC components. If sufficient evidence is found supporting data quality for use in this project, the data will be moved to the first category, but will be flagged with a "J" as per EPA specifications. Data falling into the third category (or moved there after being placed in the second category and reviewed) will not be reported in electronic data deliverables for upload to GeoTracker GAMA, but will be included and discussed in narrative reports to the Central Coast Water Board Contract Manager.

21.0 VERIFICATION AND VALIDATION METHODS

In addition to the MQOs presented in Tables 5 and 7, the standard data validation procedures documented in FGLs Quality Assurance Manuals will be used to accept, reject, or qualify the data generated by the laboratory. Laboratory personnel will verify that the measurement process was "in control" (i.e., all specified MQOs were met or acceptable deviations explained) for each batch of samples before proceeding with the analysis of a subsequent batch. In addition, each laboratory will establish a system for detecting and reducing transcription and/or calculation errors prior to reporting data.

When QA requirements have not been met, the samples will be reanalyzed when possible and only the results of the reanalysis will be submitted, provided they are acceptable. Data that does not meet the MQOs following any necessary reanalysis are not acceptable and will not be reported for in the electronic data deliverables format for upload to GeoTracker GAMA, but will be provided within the laboratory report and included and discussed in narrative reports to the Central Coast Water Board Contract Manager. FGL's QA Director will be responsible for validating data generated by the laboratory. The Tetra Tech QA Manager will be responsible for verification of data submitted by FGL, including electronic data reports, and for qualifying all data based on the evaluation of field and laboratory quality control samples and based on the QA guidelines in this QAPP. The Tetra Tech QA Manager will contact the FGL QA Director should QC issues be identified and work with them to resolve any data and or procedures that are not consistent with the QC measures described in this document.

All data reported for this project will be assessed for errors in transcription, calculation, and computer input. Field data will be entered electronically and verified against the sampling forms. Laboratory data will be reviewed by the FGL QA Director to assure that the QC program requirements in this QAPP have been met. Finally, the Tetra Tech QA Manager will provide an additional data verification and validation assessment. This review should address all QC requirements entered so as to allow for a full audit of data quality. Should an outlier or other questions arise with the data, the FGL QA Director will be contacted and the data will be verified. When the Tetra Tech QA Manager is satisfied with the accuracy of the laboratory data in question, the data will then be submitted electronically.

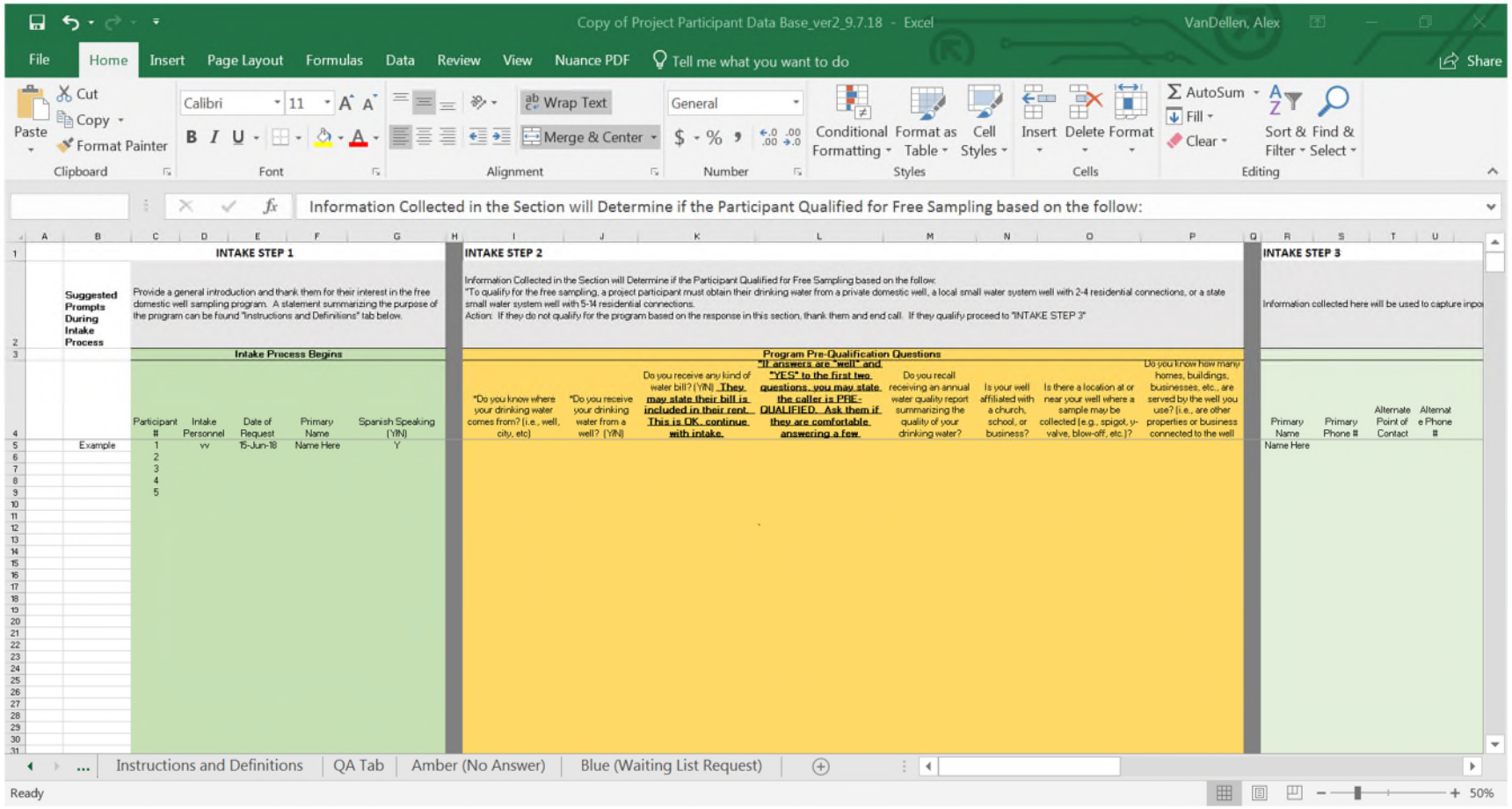
22.0 RECONCILIATION WITH USER REQUIREMENTS

The goal of the project is to provide free groundwater sampling and analytical services to domestic well and small non-public water system well owners and enable them to make decisions about the safety of their drinking water. In addition, to better inform the Central Coast Water Board, local agencies, and general public about these issues. Any uncertainty in the data will be addressed during the data validation procedures. Limitations on data use will be flagged accordingly in the database.

23.0 REFERENCES

United States Environmental Protection Agency
2001 *EPA Requirements for Quality Assurance Plans.* EPA QA/R-5. March.

A PROJECT PARTICIPANT DATABASE


Copy of Project Participant Data Base_ver2_9.7.18 - Excel
VanDellen, Alex
File
Home
Insert
Page Layout
Formulas
Data
Review
View
Nuance PDF
Tell me what you want to do
Share
Paste
Cut
Copy
Format Painter
Calibri
11
Wrap Text
General
Merge & Center
Conditional Formatting
Format as Table
Cell Styles
Insert
Delete
Format
AutoSum
Fill
Clear
Sort & Filter
Find & Select
Clipboard
Font
Alignment
Number
Styles
Cells
Editing
Information Collected in the Section will Determine if the Participant Qualified for Free Sampling based on the follow:
INTAKE STEP 1
INTAKE STEP 2
INTAKE STEP 3
Suggested Prompts During Intake Process
Provide a general introduction and thank them for their interest in the free domestic well sampling program. A statement summarizing the purpose of the program can be found "Instructions and Definitions" tab below.
Information Collected in the Section will Determine if the Participant Qualified for Free Sampling based on the follow:
"To qualify for the free sampling, a project participant must obtain their drinking water from a private domestic well, a local small water system well with 2-4 residential connections, or a state small water system well with 5-14 residential connections.
Action: If they do not qualify for the program based on the response in this section, thank them and end call. If they qualify proceed to "INTAKE STEP 3"
Information collected here will be used to capture inpo
Intake Process Begins
Program Pre-Qualification Questions
Participant #
Intake Personnel
Date of Request
Primary Name
Spanish Speaking (Y/N)
*Do you know where your drinking water comes from? (i.e., well, city, etc)
*Do you receive your drinking water from a well? (Y/N)
Do you receive any kind of water bill? (Y/N) They may state their bill is included in their rent. This is OK, continue with intake.
*If answers are "well" and "YES" to the first two questions, you may state the caller is PRE-QUALIFIED. Ask them if they are comfortable answering a few
Do you recall receiving an annual water quality report summarizing the quality of your drinking water?
Is your well affiliated with a church, school, or business?
Is there a location at or near your well where a sample may be collected (e.g., spigot, y-valve, blow-off, etc.)?
Do you know how many homes, buildings, businesses, etc., are served by the well you use? (i.e., are other properties or business connected to the well
Primary Name
Primary Phone #
Alternate Point of Contact
Alternat e Phone #
Example
1
vv
15-Jun-18
Name Here
Y
Name Here
2
3
4
5
Instructions and Definitions
QA Tab
Amber (No Answer)
Blue (Waiting List Request)
Ready
50%

B CENTRAL COAST DOMESTIC WELL FIELD SAMPLING FORM

Central Coast Domestic Well Field Sampling Form (CONFIDENTIAL)

Sample Collection Date: **Sample Collection Time (Military):**

Sampling Personnel:

SITE INFORMATION AND OBSERVATIONS

Site Address: **# of Residences Served by Well:**

POC Phone #:

POC Name: **Weather:**

Surrounding Land Use(s): Latitude:

Well Location (description): Longitude:

Survey Notes (offsets, tree cover, etc.):

Well Description (submersible pump & motor, exposed motor, etc):

Treatment System (circle one): Yes No **Description/Location:**

Well head, sampling location* and treatment system photo-documentation (circle one): Yes No

WELL STABILIZATION

(record field measurements and await parameter stabilization before sampling*)

Well Depth (ft): **Instrument ID:**

Time (min)	Water Temp ('C)	SC (us/cm)	pH	DO (mg/L)	Comments (clarity, etc)

Parameter	Stability Criteria
pH	± 0.1 pH units
Sp. Cond.	± 3% us/cm
DO	± 0.5 mg/L

Site Notes:

GEOTRACKER WELL AND SAMPLING INFORMATION DATA FIELDS

Project Name: CC Domestic Well Project

Global ID: T10000010346

Field Point Name[1]: CCDW_____

Log Code: TTSM

Field Point Class[2] (check box below):

□ PRIW □ LSMWS □ SSMWS

Field Point Description*[3] (check box below):

□ Well Head □ Distribution System

Analyte	Sample Container/Volume
TDS, alkalinity as CaCO3, sulfate, chloride	Poly / 1 Quart
Nitrate as N	Poly 1/2 pint
Calcium, magnesium, sodium, potassium, arsenic	Poly / 250 mL
1,2,3-Trichloropropane	4X40 mL VOAs
Chromium VI	Poly 1/2 pint
Perchlorate	Poly 1 pint ****Fill Half Full, Agitate, Then Place on Ice****

Quality control sample(s) collected at this location? (check all that apply): □ QCFB □ Duplicate

NOTES

***Samples should be collected before any treatment/filtration and as close to the well head as possible; preferably before the pressure tank and distribution system (see Section 6.4.2.3 of the QAPP)!**

1 **Field Point Name** (one per well/sample location):
CCDW#, where "#" represents residence/well numbering sequence 1, 2, 3, etc. up to 9999, and CCDW#W# for residences or local/state small water systems with multiple wells where the second "W#" represents the well

2 **Field Point Class**:
- "PRIW" (Private Domestic Drinking Water Well; single connection)
- "LSMWS" (Local Small Water System; 2-4 service connections)
- "SSMWS" (State Small Water System; 5-14 service connections)

3 **Field Point Description (sampling location)**:
- "Well Head" (collected directly from well or well head)
- "Distribution System" (collected downstream of well head before any treatment)

C EXAMPLE LABORATORY PACKAGE SUBMITTAL

Central Coast Regional Water Quality Control Board

YOUR DRINKING WATER TEST RESULTS AND SUPPORTING INFORMATION

Dear Central Coast Drinking Water Well Testing Program Participant,

Thank you for participating in the Central Coast Water Board's Drinking Water Well Testing Program. This package includes the testing results for your well.

Please review the attached report. If any of your results are marked as "fail", we advise you re-test your well. We also advise using a certified[1] laboratory to confirm the results.

For more information, visit www.centralcoastwelltesting.org where you can,

- Find certified laboratories near you,
- Download a free well owner's guide,
- Learn more about well drinking water quality.

If all your results are marked as "pass", please continue to test your well regularly.

You may have health-related questions. If so, please contact your doctor or public health agency.

For well testing program questions, please contact Julia Dyer at Julia.Dyer@waterboards.ca.gov or (805) 542-4624.

Sincerely,

Julia Dyer
Senior Environmental Scientist (Specialist)

Enclosures:
FGL Laboratory Report

[1] California Environmental Laboratory Accreditation Program (ELAP) certified laboratory

D EXAMPLE CHAIN-OF-CUSTODY FORM

ENVIRONMENTAL FGL AGRICULTURAL
Analytical Chemists

www.fglinc.com

CHAIN OF CUSTODY
AND ANALYSES REQUEST FORM

CLIENT DETAILS — SECTION I

Client: Tetra Tech, Inc.

Customer Number: 2026198

3201 Airpark Dr.

Suite 108

Santa Maria CA 93455

Phone: 805-739-2661 **FAX:** 805-739-2605

Email: alex.vandellen@tetratech.com

Project Name: Central Coast Domestic Well Project

Geotracker Global ID: T10000010346

Contact Person: Alex Van Dellen, Tetra Tech Project Manager

LogCode: TTSM

SAMPLING — SECTION II

Lab Number:

Time:

Shipping Charge:

Sampler(s):

Mileage:

Pickup Charge:

SAMPLE INFORMATION — SECTION III

ANALYSES REQUESTED

Samp Num	Field Point Name	Sample ID	Date Sampled	Time Sampled	DW Well (DW) DW + Irr. Well (B)	1,2,3 -Trichloropropane 40mL VOA X4 (no pres)	Chromium VI 8oz(P) w/ pres buffer, Fill 3/4 Full, Agitate, Then Place on Ice	Perchlorate ****Fill Half Full, Agitate, Then Place on Ice**** 1Pint (no pres)	Wet Chemistry-SO4,TDS,Cl,Alk. (CaCO3) 32oz(P)	Wet Chemistry-Nitrate as N 8oz(P)-H2SO4	Metals, Total -Ca, Mg, K, Na, As 250ml(P)-HNO3	Field pH	Field Specific Conductivity (mS/cm)	Electronic Data Transfer (GeoTracker)	Notes
0	Travel Blank	Travel Blank	28-Aug-17	1330		2								X	
1	CCDW1W1	CCDW1W1	28-Aug-17	1330		4	1	1	1	1	1			X	
2	CCDW2W1	CCDW2W1	28-Aug-17	1358		4	1	1	1	1	1			X	
3	CCDW3W1	CCDW3W1	28-Aug-17	1425		4	1	1	1	1	1			X	
4	CCDW4W1	CCDW4W1	28-Aug-17	1450		4	1	1	1	1	1			X	
5	CCDW4W1	CCDW4W1DUP	28-Aug-17	1508		4	1	1	1	1	1			X	
6	QCFB	QCFB	28-Aug-17	1525		4								X	
														X	
														X	
														X	
														X	
														X	

REMARKS — SECTION IV

DO UPLOAD RESULTS TO
GEOTRACKER UNTIL APPROAVED
BY TETRA TECH QA REP

CUSTODY — SECTION V

Relinquished By:	**Print Name:**	**Date:**	**Time:**
Relinquished By:	**Print Name:**	**Date:**	**Time:**
Relinquished By:	**Print Name:**	**Date:**	**Time:**
Relinquished By:	**Print Name:**	**Date:**	**Time:**

Corporate Office and Laboratory
853 Corporation Street
Santa Paula, CA 93060
Tel: (805) 392-2000
FAX: (805) 525-4172

Office Laboratory
3442 Empresa Drive, Suite D
San Luis Obispo, CA 93401
Tel: (805) 783-2940
FAX: (805) 783-2912

E LABORATORY QUALITY ASSURANCE PROJECT PLAN

Fruit Growers Laboratory, Inc.
QA Manual
California ELAP

Prepared by

David Terz
Quality Assurance Director

QUALITY MANUAL IDENTIFICATION AND APPROVALS

Document Title: FGL Quality Manual
Revision ID: 16E
Revision Date: 06/19/2013

Quality Manual Approvals

Approved by:

Name: Kelly A. Dunnahoo
Title: President/Lab Director
Signature: _____
Date: 6-27-13

Name: David E. Terz
Title: Quality Assurance Director
Signature: _____
Date: 6.27.13

1.0 COMPANY INTRODUCTION

1.1 Company Identification:

1.1.1 Name: Fruit Growers Laboratory, Incorporated (aka FGL Environmental or FGL)

1.1.2 **Corporate Headquarters/Laboratory-Santa Paula:**
1.1.2.1 Laboratory Director: Kelly Dunnahoo
1.1.2.2 Quality Assurance Director: David Terz
1.1.2.3 Address: 853 Corporation Street, Santa Paula, CA 93060
1.1.2.4 Phone: 805-392-2000
1.1.2.5 Fax: 805-525-4172
1.1.2.6 Website: www.fglinc.com
1.1.2.7 Certifications
1.1.2.7.1 ELAP No. 1573
1.1.2.7.2 NELAP No. 01110CA

1.1.3 **Laboratory-Stockton**
1.1.3.1 Laboratory Manager: Jim Kavanaugh
1.1.3.2 Address: 2500 Stagecoach Road, Stockton, CA 95215
1.1.3.3 Phone: 209-942-0182
1.1.3.4 Fax: 209-942-0423
1.1.3.5 Website: www.fglinc.com
1.1.3.6 Certifications: ELAP No. 1563

1.1.4 **Laboratory-Chico**
1.1.4.1 Laboratory Manager: Chris Iden
1.1.4.2 Address: 563 Lindo Avenue
1.1.4.3 Phone: 530-343-5818
1.1.4.4 Fax: 530-343-3807
1.1.4.5 Website: www.fglinc.com
1.1.4.6 Certifications: ELAP No. 2670

1.1.5 **Laboratory-San Luis Obsipo**:
1.1.5.1 Laboratory Manager: Jayna Kostura
1.1.5.1 Address: 3442 Empressa Drive, Suite D
1.1.5.2 Phone: 805-783-2940
1.1.5.3 Fax: 805-783-2912
1.1.5.4 Website: www.fglinc.com
1.1.5.5 Certifications: ELAP No. 2775

1.1.6 **Laboratory-Visalia:**
1.1.6.1 Laboratory Manager: Neil Jessup
1.1.6.1 Address: 9415 W. Goshen Avenue, Visalia, CA 93291
1.1.6.2 Phone: 559-734-9473
1.1.6.3 Fax: 559-734-8435
1.1.6.4 Website: www.fglinc.com
1.1.6.5 Certifications: ELAP No. 2810

1.2 Company Overview

Fruit Growers Laboratory, Inc. is a full service agronomic and environmental laboratory. The laboratory will be referred to throughout this plan as FGL.

FGL's organization consists of its primary laboratory and corporate offices in Santa Paula, and satellite

laboratories in San Luis Obispo, Stockton, Chico and Visalia. The corporation employs approximately 90 employees statewide. FGL is classified as a small business for federal projects and a large business for State of California projects. The Standard Industrial Classification (SIC) code is 8734.

1.3 Company History

FGL was established in 1925 as a Cooperative enterprise providing agronomic laboratory services to Sunkist contracted growers in California. Sunkist Growers (a cooperative) is a grower owned agricultural marketing organization.

In 1927 FGL secured it's drinking water state certification and since then has provided this service to drinking water purveyors throughout the state. In 1973 Fruit Growers Laboratory was reincorporated as a standard California corporation and continued to expand its services to the environmental and agronomic industries. FGL provides environmental and agricultural analytical support services to a variety of clients out of both our laboratories. These include drinking water purveyors, wastewater and hazardous waste generators and handlers, farming groups, individuals growers, private companies, prime government contractors, municipalities, state and federal agencies. A substantial proportion of our business is made up of a large number of small clients thus distributing our business over a large base of customers. This helps prevent a small number of larger clients dominating our total business.

2.1 Quality Assurance Policy Statement

FGL Environmental's Quality Assurance Policy

"Management and staff are committed to providing analytical services that are scientifically valid, legally defensible and of known precision and accuracy in order to meet or exceed the definitions and expectations of quality of our clientele."

2.2 Purpose

The FGL Quality Manual (QM) serves as an operational charter for the company. It defines the purpose, structure and operating principles of the laboratory and presents an overview of the primary factors of the quality assurance system.

This QM has been prepared according to guidelines presented in the 22 CCR 64815 (b).

2.3 Scope

This QM applies to the services supporting, and generation of, analytical data for all of FGL's laboratories . As most environmental client needs are driven by various federal and state regulations, the plan has been designed to meet the requirements of the following services and programs:

a) Analysis of Drinking Water supplies in support of the Safe Drinking Water Act (SDWA)

b) Analysis of waste stream samples in accordance with National Pollution Discharge Elimination System/Clean Water Act requirements.

c) Analysis and characterization of soil, water and waste samples per the Resource Conservation and Recovery Act (RCRA) for compliance or disposal purposes.

d) Analysis and characterization of soil, water and waste samples for site assessment purposes.

2.4 Service and Data Integrity Policy

FGL recognizes that maintaining a proper ethical standard is an important element of an effective QM. In order to ensure that all personnel understand the importance the company places on maintaining high ethical standards at all times, FGL has established a "Service and Data Integrity Policy" and it is presented as Figure 2.1 on the following page for your information. This policy is used to set the standard within the organization. Each employee is required to sign the policy, signifying agreed

compliance with it's stated purpose. Copies of all signed ethics policy statements are maintained in the QA personnel files.

Figure 2.1 Service and Data Integrity Policy

Service and Data Integrity Policy

Fruit Growers Laboratory Incorporated or FGL Environmental's business is to provide analytical data and support services to its customers. **Each employee of FGL plays a vital role in performing this task.**

Providing a service of superior quality and integrity is impacted by three primary factors:

1) FGL management's commitment to, and support of staff in, providing service and data of quality and
2) Each employee's personal commitment to provide a service of quality and integrity.
3) Each employee's personal skill and knowledge, gained through education and experience, relating to the

When these three factors are optimized the service being provided will be exceptional.

FGL is pledging its full commitment and support to helping you provide the best possible service to our customers. To uphold this policy, FGL will provide the following:

1) the right to "stop the assembly line" when a problem or error is discovered.
2) a company wide training program to augment your education and/or experience and to provide you with
3) a management "open door policy" is extended to all employees with a guarantee of no reprisal.

This ensures that each employee has the opportunity and the obligation to be a part of FGL's mission to provide the best possible level of analytical service.

As an employee of FGL, integrity in providing service and data must be the highest priority. Service or data quality problems must be immediately brought to the attention of your manager and/or supervisor for review and to initiate solutions to legitimately satisfy the customers' expectations. Ignoring a problem or the falsification of data or information cannot be tolerated since it could significantly impact the reputation and the long term viability of our customers and FGL Environmental.

In our efforts to provide excellent service and high quality defensible analytical data, FGL strives to employ staff of the highest character and personal integrity. Any staff member that knowingly deviates from this expectation of integrity compromises, not just his or her own position, but that of his/her colleagues and will be subject to immediate discharge.

I have read and understand the above information and agree to abide by this policy. I further understand that nothing contained in this policy alters my at-will employment relationship with FGL Environmental.

Employee Name:_____

Signature:_____ Date:_____

3.0 MANAGEMENT AND ORGANIZATION

This is primarily referenced from 22 CCR 64815 (b).

The primary objective of the QM is to ensure that systems are in place so that the Quality Assurance Policy Statement is achieved. The management of FGL is committed to the execution of the QM to enable this objective. The company officers, lab directors and managers are required to comply with the program's requirements and responsibilities.

3.1 Management Responsibility and Authority

The following provides a listing of responsibilities and authority of key managerial personnel involved in laboratory analysis and oversight of the QM:

a) Laboratory Director

1) Responsibility

i. Ensure that the lab is organized in such a way that confidence in its independence of judgment and integrity is maintained at all times.
ii. Establish the scope of this QM and implementing, assessing and continually improving an effective quality system.
iii. Specify the responsibility, authority and interrelationships of all personnel who manage, perform or verify work affecting the quality of calibrations and tests.
iv. Ensure that managers have overall responsibility for the technical operation of the laboratory, comply with the QM and require compliance by all personnel.
v. Ensure that directors and managers have the necessary authority and resources in which to achieve the above.
vi. Ensure supervision by persons familiar with the calibration or test methods and procedures, the objective of the calibration or test and the assessment of the results. The ratio of supervisory to non-supervisory personnel is such that adherence to laboratory procedures and accepted techniques is maintained.
vii. Ensure that FGL personnel are free from any commercial and other undue pressures which might adversely affect the quality of their work.
viii. Ensure that adequate review of new contracts are performed to verify that FGL has the appropriate facilities and resources to commence work.

2) Authority

i. Authority to council and terminate employees for dishonesty, unacceptable work behavior or non-compliance with established QA policies and procedures.
ii. Authority is granted from the president of FGL.

b) Laboratory/Department Manager(s)

The division managers for technical areas of the lab are considered to be technical directors and have overall responsibility for technical operations of the laboratory.

1) Responsibility

i) Ensure that personnel with appropriate educational and/or technical background perform all tests for which the laboratory is accredited.
ii) Ensure compliance with methods and procedures as written.
iii) Ensure that analytical procedures are performed in accordance with the requested methods and SOP's.
iv) Oversee prioritizing of work and perform client contact regarding analyses and data interpretation.

v) Ensure that adequate review of new contracts are performed to verify that FGL has adequate technical capabilities to commence work.
vi) Oversee preparation of analytical reports and data review.

2) Authority
i) Authority to council and terminate employees for dishonesty, unacceptable work behavior or non-compliance with established QA policies and procedures.
ii) Authority to perform client contact and, where necessary, remediate complaints.
iii) Authority is granted from the Laboratory Director.

c) Quality Assurance Director

The Quality Assurance Director has direct access to technical directors and to the highest level of management at which decisions are taken on laboratory policy and resources. The Quality Assurance Director serves as the focal point for QA/QC for all the FGL laboratories and is independent from the laboratory functions and influence.

1) Responsibility
i) Responsible for the QM and its implementation including recommending pertinent additions to the QM.
ii) Responsible for monitoring and assessing compliance of the laboratory with the requirements contained in the QM.
iii) Conducts annual audits and inspections to assess compliance with established methods, policies and procedures.
iv) Maintains a document control system, containing current policies and procedures utilized by the company, to ensure that all documents clearly indicate the time period and locations in which the procedure or policy was in force.
v) Maintains various analytical certifications for the laboratory.
vi) Reviews laboratory performance on performance evaluation studies submitted to FGL by clients and regulatory agencies.
vii) Responsible for the oversight and/or review of the quality control data.
viii) Investigates all inquiries relative to data quality issues and does follow up on corrective actions where necessary.
ix) Ensures that adequate review of new contracts are performed to verify that FGL has an adequate Quality Assurance program to commence work.
x) Prepares and issues reports to management in regard to the responsibilities listed above

2) Authority
i) The quality assurance staff have the authority to stop or change any analytical procedure in order to assure that data quality is maintained.

3.2 Organizational Charts

The following pages contain general organizational charts

Figure 3.1: Corporate Organization Chart - Fruit Growers Laboratory

June 2013

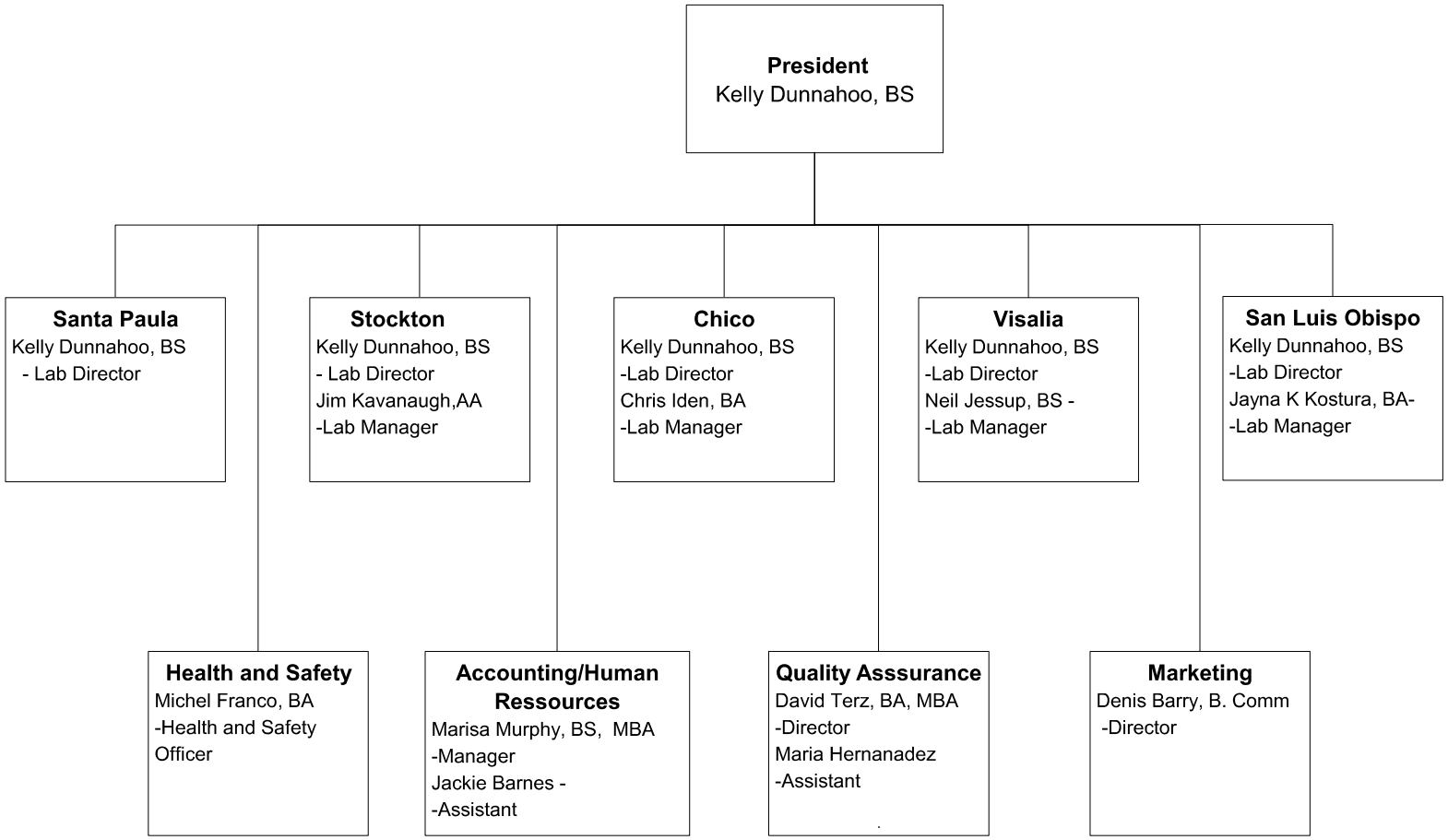


Figure 3.2: Laboratory Organization Chart - Fruit Growers Laboratory

June 2013

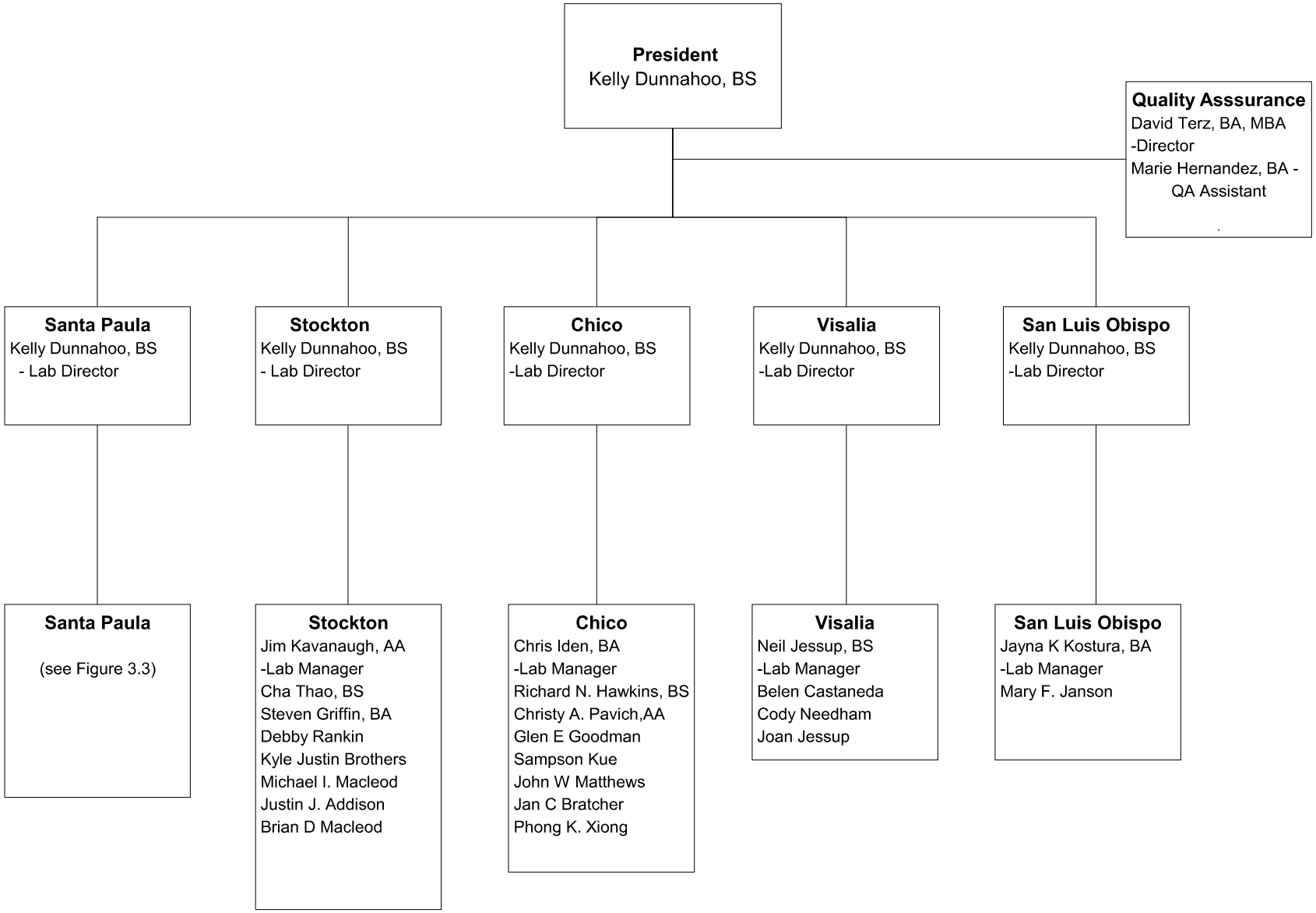
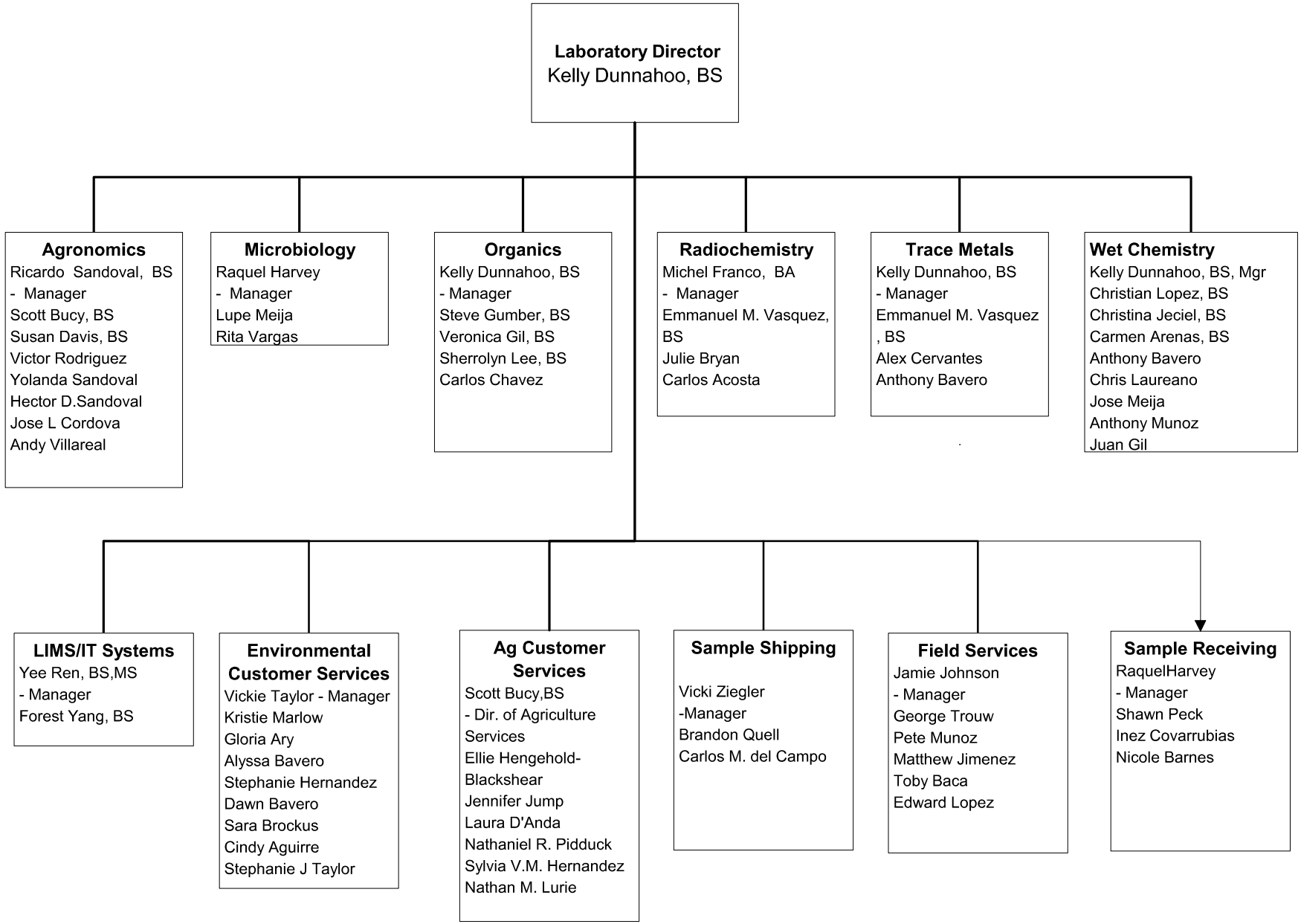


Figure 3.3 Organization Chart - Santa Paula Laboratory
June 2013



4.0 PERSONNEL

This is primarily referenced from 22 CCR 64815 (b)

4.1 General Requirements for Laboratory Staff

a) Responsibility
   1) To comply with all quality assurance/quality control requirements that pertain to their organizational/technical function.
   2) Maintain a combination of experience and education to adequately demonstrate a specific knowledge of their particular function and a general knowledge of laboratory operations, analytical test methods, quality assurance/quality control procedures and records management.

b) Authority
   1) All personnel have the authority to initiate a stop-work order where detrimental ethical, contractual, quality, safety or health conditions exist. The stop-work order must be reported to their manager.
   2) Authority is granted from the Lab Director and laborarory manager to whom they report.

4.2 Education, Experience and Training

a) Minimal levels of qualification, experience and skills necessary for all positions in the laboratory are specified in the applicable job description.

b) To ensure that all technical staff are knowledgeable in regard to basic laboratory skills, such as using a balance or mechanical pipet, training is provided to each staff member (SOP reference: 2D0900122). Such training is documented.

c) To ensure initial proficiency, each analyst will be required to perform an initial demonstration of capability (IDOC) study satisfying the requirements in the specific methods or 40 CFR 136.7(c). The IDOC can be:
   i) Preparation consisting of one Method Blank (MB) and four Laboratory Control Spikes (LCS).
   ii) In cases where no MB's or LCS's are analyzed, four Continuing Calibration Verification Standards.
   iii) In cases where i) and ii) not technically feasible, analyze real world samples in parallel with another trained analyst (i.e. Microbiology, pH).

d) To ensure that the training of the each employee is kept up-to-date, the following will be performed:
   1) Evidence will be on file that demonstrates that each employee has read, understood, and is using the most recent version of the FGL QM procedures which relate to his/her job responsibilities.
   2) Training courses or workshops on specific equipment, analytical techniques or laboratory procedures will be documented.
   3) Evidence will be on file that demonstrate that each employee has read, understands and agrees to perform the most recent version of the standard operating procedure.
   4) As part of the on-going DOC, each technical employee will be considered currently proficient by achieving at least one of the following once per year or whenever there is a significant change in instrument type or test method:
      i) Another Initial DOC
      ii) Acceptable results in a PE study
      iii) Four consecutive LCS's from the past year

4.3 Records

Records relevant to qualifications, training, skills and experience of the technical personnel will be maintained in a training file for each employee.

5.0 FACILITIES

This is primarily referenced from 22 CCR 64815 (b)

5.1 Facility descriptions

a) FGL Santa Paula occupies two buildings totaling 20,000 square feet of space. Approximately 70 percent is dedicated to the analytical laboratory functions. Separate laboratory areas are dedicated to GC/MS volatiles, GC/MS semi-volatiles, trace metals, radiochemistry, wet chemistry analysis and trace metals preparation, microbiological preparation and analysis, organic extractions, radiochemistry preparation and analysis (including defined HRAM and LRAM areas).

The GC/MS volatiles analysis area is operated in a positive pressure environment. The GC analysis area and organic extraction area is operated in a negative pressure environment. This coupled with separate HVAC systems for each area provides a contaminant free environment for trace-level volatiles analysis. The laboratory has 22 fume hoods totaling 130 linear feet of hood space.

b) FGL Stockton occupies two buildings totaling 3000 square feet of space. Approximately 50 percent is dedicated to the analytical laboratory functions. A separate laboratory area is dedicated to Microbiology.

c) FGL Chico occupies one building totaling 4000 square feet of space. Approximately 50 percent is dedicated to the analytical laboratory functions.

d) FGL San Luis Obispo occupies one building totaling 1200 square feet of space. Approximately 30 percent is dedicated to the analytical laboratory functions. A separate laboratory area is dedicated to Microbiology.

e) FGL Visalia occupies one building totaling 1800 square feet of space. Approximately 25 percent is dedicated to the analytical laboratory functions. A separate laboratory area is dedicated to Microbiology.

5.2 Working Environment

a) Laboratory test areas, energy sources, lighting, heating and ventilation are adequate to facilitate proper performance of tests.
b) The environment in which these activities are undertaken will not invalidate the results or adversely affect the required accuracy of measurement.
c) In instances where monitoring or control of items specified in a test method or by regulation, such as fume hoods and safety showers, the laboratory will meet and document adherence to the laboratory facility requirements.

5.3 Work Areas

a) FGL maintains effective separation between neighboring areas when the activities are incompatible.
b) Adequate measures are taken to ensure good housekeeping in the laboratory.
c) Work spaces are available to ensure an unencumbered work area. Work areas include:
1) access and entryways to the laboratory;

2) sample receipt area(s);
3) sample storage area(s);
4) sample preparation and testing area(s);
5) data handling and storage area(s).
6) chemical and waste storage area(s);

5.4 Security

a) All facilities have an alarm security system which is monitored by an outside company.
b) Only authorized FGL personnel have access to the facilities.

5.5 Facility Floor Plans

The following pages contain facility floor plans:
5.5.1 FGL Santa Paula Laboratory 853 Corporation Street (figure 5.1)
5.5.2 FGL Santa Paula Laboratory 801 Corporation Street (figure 5.2)
5.5.3 FGL Stockton Laboratory (figure 5.3)
5.5.4 FGL Chico Laboratory (figure 5.4)
5.5.5 FGL San Luis Obsipo Laboratory (figure 5.5)
5.5.6 FGL Visalia Laboratory (figure 5.6)

Figure 5.1: Santa Paula Laboratory - 853 Building

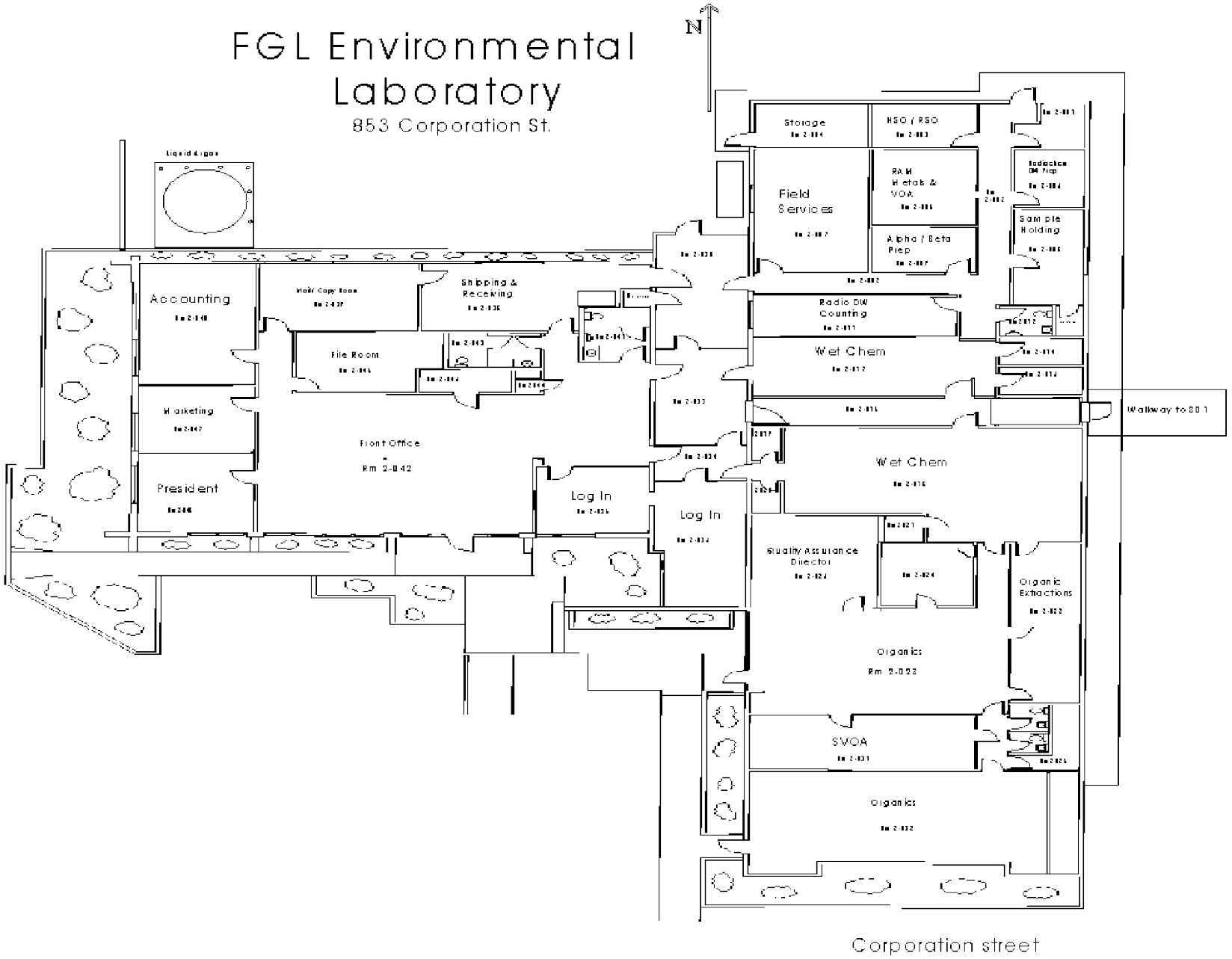
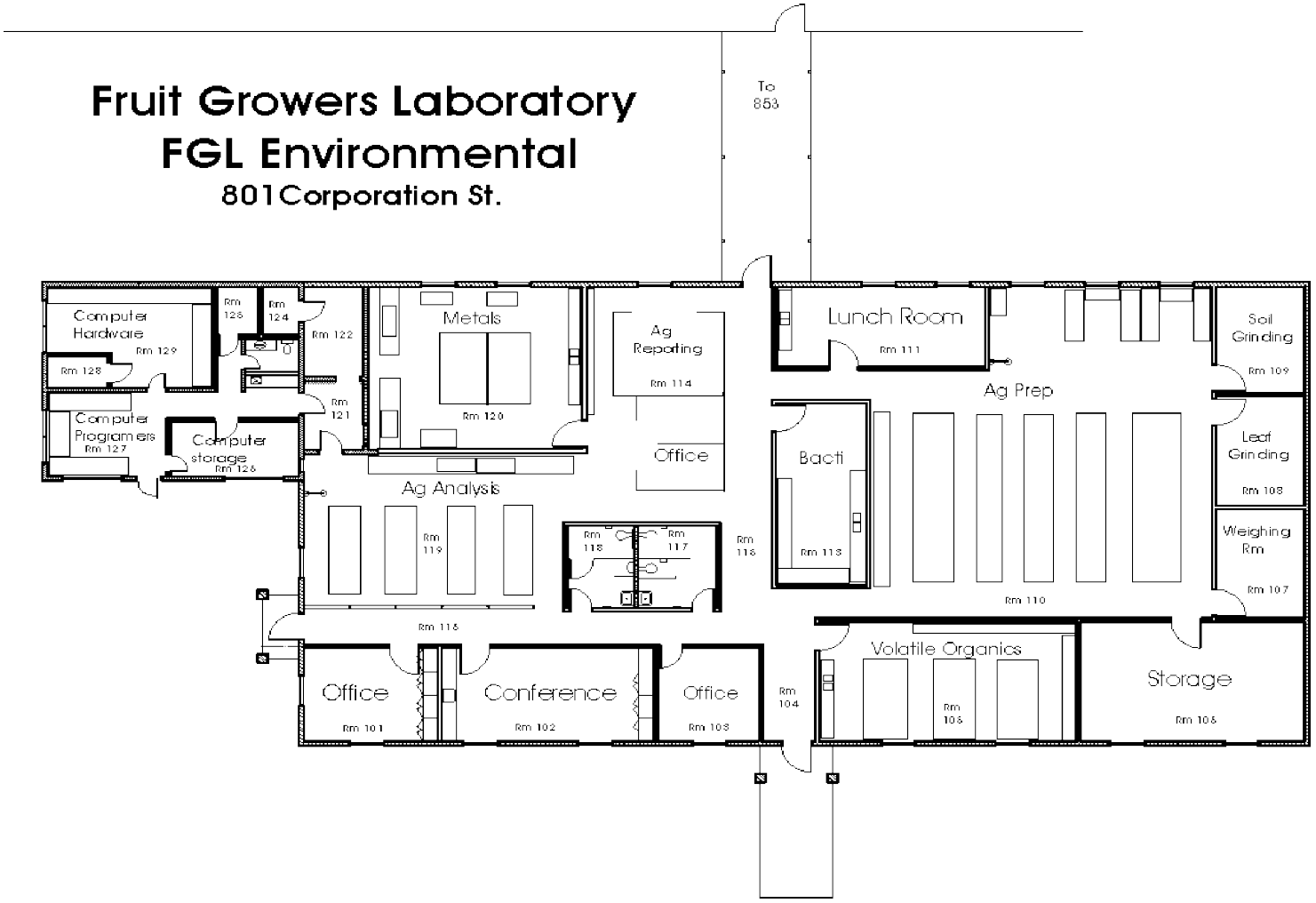
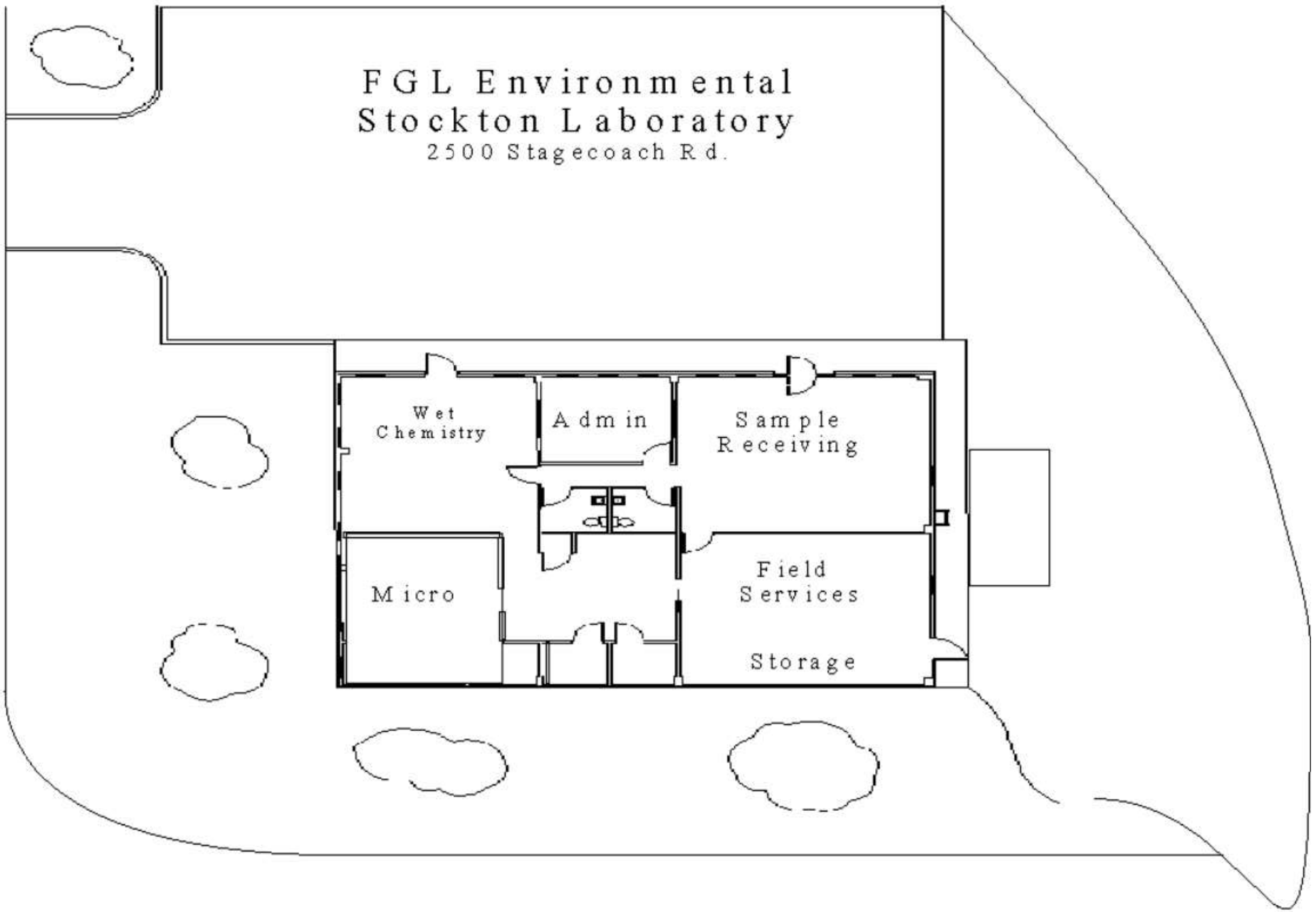
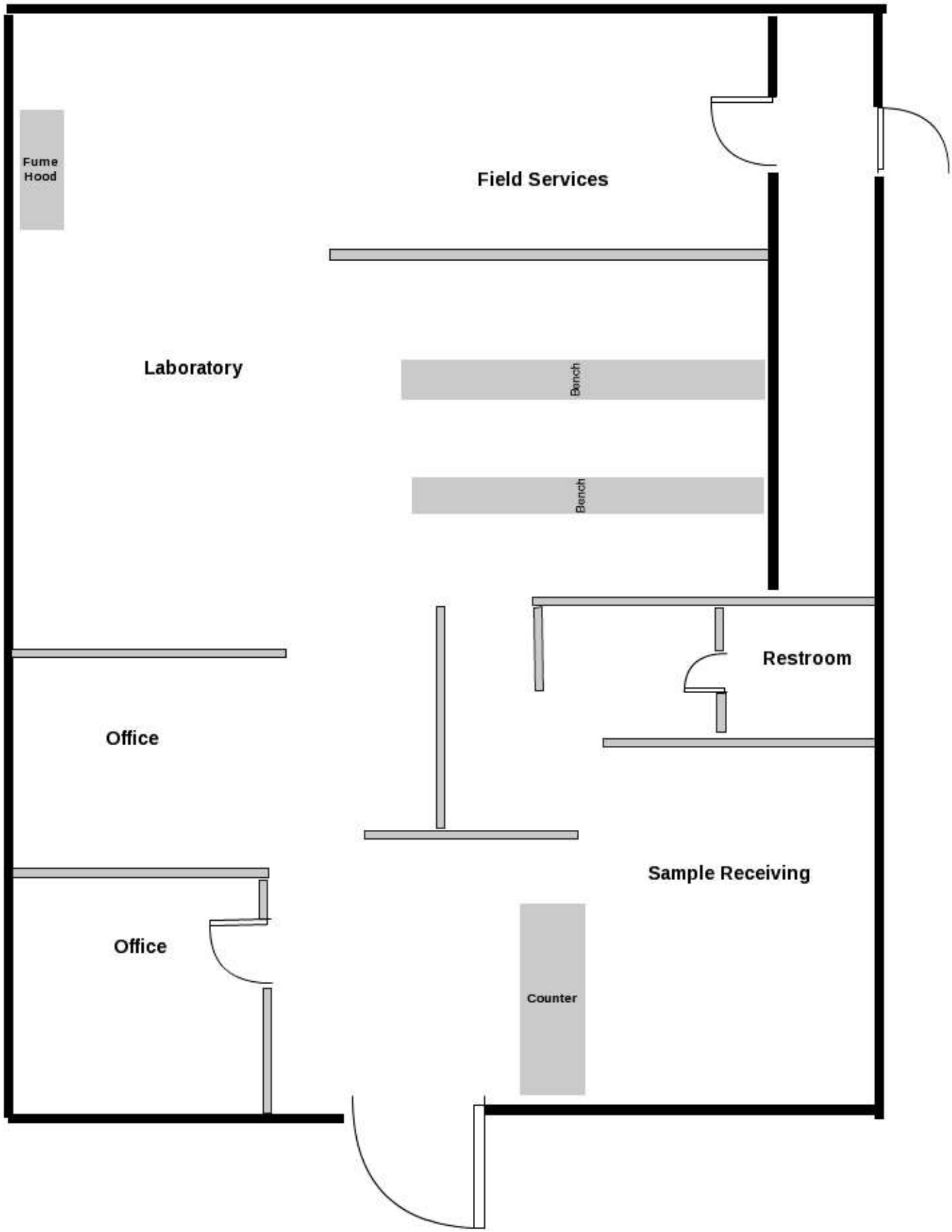
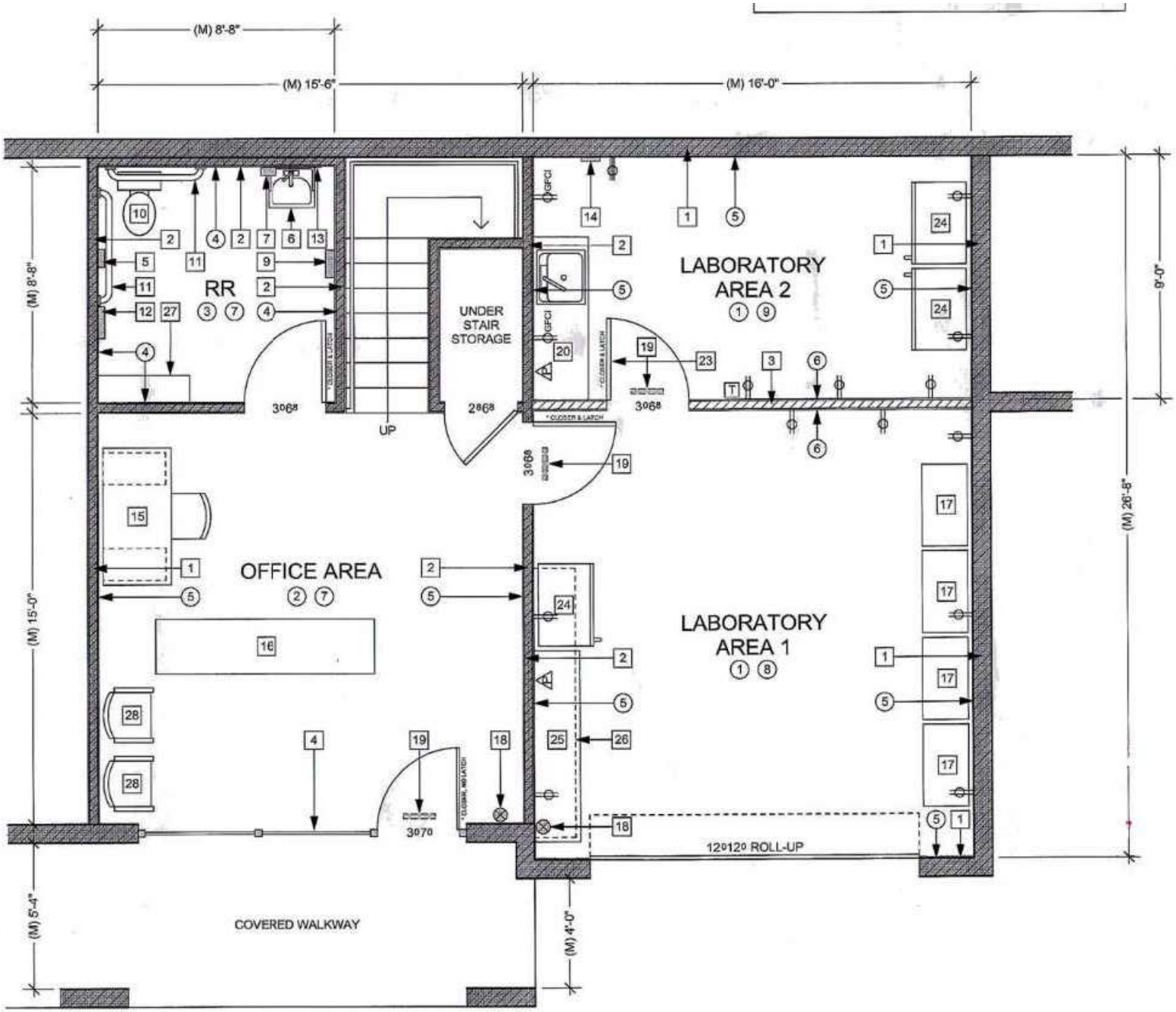


Figure 5.2: Santa Paula Laboratory - 801 Building

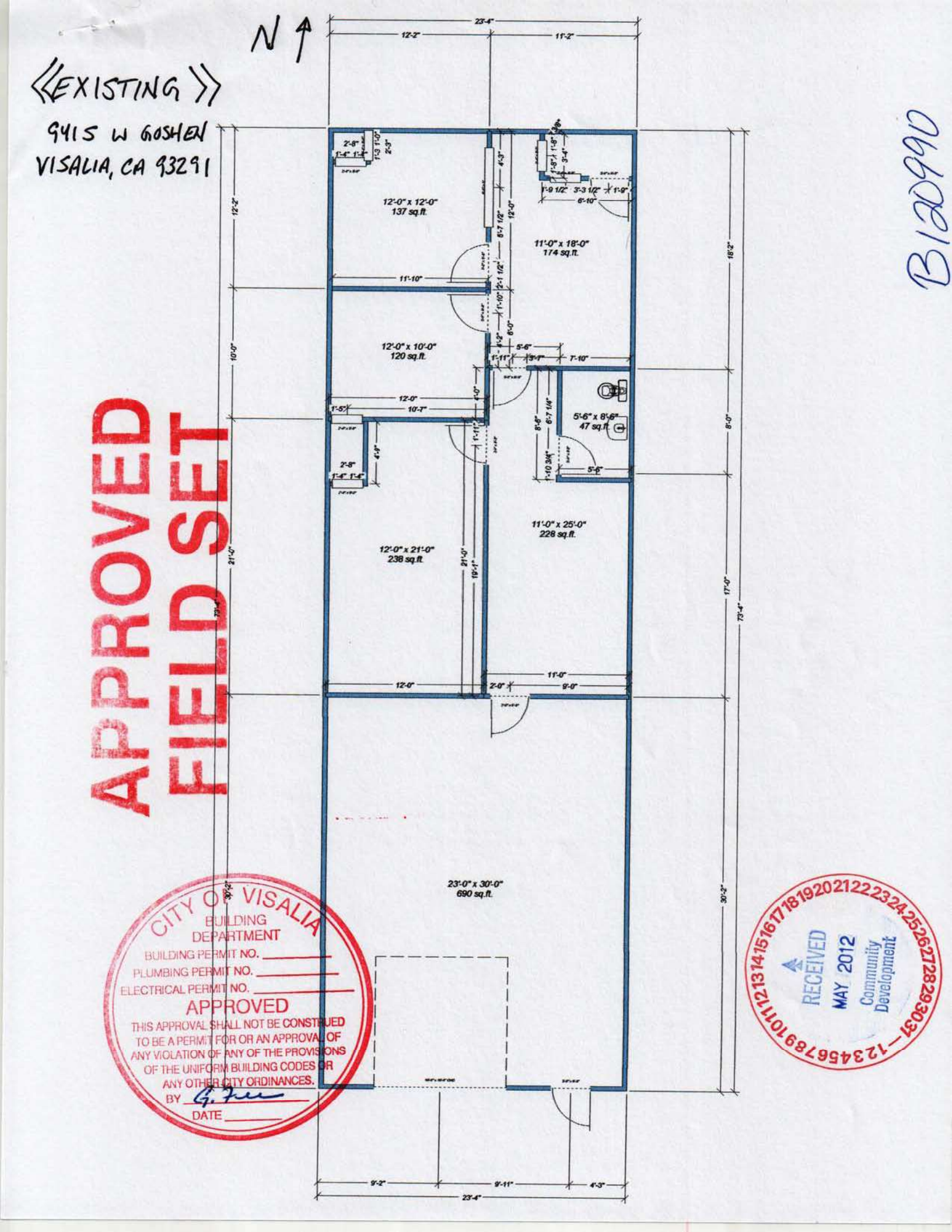



FGL Environmental
Stockton Laboratory
2500 Stagecoach Rd.
Wet Chemistry
Admin
Sample Receiving
Micro
Field Services
Storage


Fume Hood
Field Services
Laboratory
Bench
Bench
Restroom
Office
Sample Receiving
Office
Counter


(M) 8'-8"
(M) 15'-6"
(M) 16'-0"
(M) 8'-8"
(M) 15'-0"
(M) 5'-4"
(M) 4'-0"
(M) 26'-8"
8'-0"
RR
UNDER STAIR STORAGE
UP
LABORATORY AREA 2
OFFICE AREA
LABORATORY AREA 1
COVERED WALKWAY
12'0"12'0" ROLL-UP
3068
2868
3070
GFCI
CLOSER & LATCH

FLOOR PLAN


N
«EXISTING»
9415 W GOSHEN
VISALIA, CA 93291
APPROVED
FIELD SET
12'-0" x 12'-0"
137 sq.ft.
11'-0" x 18'-0"
174 sq.ft.
12'-0" x 10'-0"
120 sq.ft.
5'-6" x 8'-6"
47 sq.ft.
11'-0" x 25'-0"
228 sq.ft.
12'-0" x 21'-0"
238 sq.ft.
23'-0" x 30'-0"
690 sq.ft.
CITY OF VISALIA
BUILDING DEPARTMENT
BUILDING PERMIT NO.
PLUMBING PERMIT NO.
ELECTRICAL PERMIT NO.
APPROVED
THIS APPROVAL SHALL NOT BE CONSTRUED TO BE A PERMIT FOR OR AN APPROVAL OF ANY VIOLATION OF ANY OF THE PROVISIONS OF THE UNIFORM BUILDING CODES OR ANY OTHER CITY ORDINANCES.
BY
DATE
RECEIVED
MAY 2012
Community Development
B12-0990

6.0 QUALITY SYSTEMS

This is primarily referenced from 22 CCR 64815 (b).

6.1 Audits

a) Internal Audits

The QM can only accomplish its objectives if management and personnel are committed to adherence to the program. In order to assess continued compliance and to identify strong and weak points within the plan, the FGL QA department performs annual internal audits . Such audits are carried out by the quality assurance director or designee(s) who are trained and who are, wherever possible, independent of the activity to be audited. Where the audit findings cast doubt on the correctness or validity of the laboratory's calibrations or test results, the laboratory will take immediate corrective action and will immediately notify, in writing, any client whose work may have been affected.

b) External Audits

External audits are routinely on a bi-annual basis by regulatory agencies such as California Department of Health Services. Client audits are also performed in order to verify compliance with client quality and contractual specifications.

c) Performance Audits

In addition to the audits listed above, FGL ensures the quality of results provided to clients by implementing checks to monitor the quality of the laboratory's analytical activities. Examples of such checks are:

1) internal quality control procedures using regulatory requirements or, whenever possible, statistical techniques (see section 6.3);
2) participation in proficiency testing or other inter-laboratory comparisons. FGL currently participates in the following studies:
    i) Water Supply (WS), including Microbiology, annual
    ii) Water Pollution (WP), including Microbiology, annual
    iii) Soil/UST, annual
3) correlation of results for different parameters of a sample
    i) cation-anion balance
    ii) TDS/EC ratio
    iii) Ammonia less than/equal to TKN
    iv) Total results greater than dissolved results
    v) Carbonaceous BOD less than BOD

6.1.1 Audit Review

All audit findings and any corrective actions that arise from them are documented. The laboratory management will ensure that these actions are discharged within the agreed time frame.
The annual quality assurance report to management summarizes or verifies the following functions:

1) performance evaluation study summaries;
2) water quality monitoring summary;
3) equipment status
4) lab certification status
5) audit schedules

6.2 Corrective Actions

a) FGL has implemented non-conformance procedures to be followed when departures from documented policies, procedures and quality control have occurred. This requires the use of a non-conformance report (or similar form such as the report/invoice amendment cover letter) which may require corrective action. This procedure is outlined in the Non-conformance/Corrective Action Program (SOP reference: 2D0900105). These procedures include but are not limited to the following:
   1) assign a unique non-conformance tracking number to track the non-conformance and, if necessary, the corrective action to final closure;
   2) identifying the department in which the non-conformance occurred;
   3) identifying the type of non-conformance which occurred, such as calibration failure, standard expiration or reporting;
   4) record the pertinent details of the non-conformance, such as analytical method, batch ID, failure and probable cause;
   5) quality assurance review to track the non-conformance and determine whether a corrective action will be required.

b) If a corrective action is deemed necessary the following procedures are performed:
   1) identify the individual(s) responsible for performing the corrective action;
   2) identify the remedial actions (short term) taken to prevent a similar non-conformance from occurring;
   3) identify the corrective actions (long term) taken to prevent a similar non-conformance from occurring;
   4) quality assurance review to verify the corrective actions taken are adequate;
   5) quality assurance closure of the corrective action upon approval.

6.3 Essential Quality Control Procedures

The following essential quality controls, based on analytical methods and 40 CFR 136.7 , are utilized, where applicable, for all test methods performed at FGL. The manner in which they are implemented is dependent on the type of test. FGL considers certain quality controls as “critical to data defensibility” and other quality controls as “information only.” Quality controls considered to be “critical to data defensibility” are calibration blanks, calibration verifications, method blanks and LCS’s. In cases where controls “critical to data defensibility” fail, wherever possible, samples will be reprepared and/or analyzed to obtain acceptable data. If this is not possible the client will be notified of the failure and an acceptable resolution determined. In the cases of failing “information only” controls, the information will be provided to the client for their review and evaluation. Table 7.1 contains a comprehensive list of quality control types used by FGL (noted as “critical to data defensibility” and “information only”).

a) FGL has protocols in place to provide and/or monitor the following quality controls:

   1) positive and negative controls to monitor sample preparation methods such as Method Blanks and Laboratory Control Samples (LCS), Matrix Spikes (MS), Surrogates (Surr);
   2) measures to evaluate analytical variability/reproducibility, such as Matrix Spike Duplicates (MSD’s) or Laboratory Duplicates (Dup’s) (Note: the samples used for these quality controls are selected by the analyst);
   3) measures to evaluate test method capability, such as Demonstration of Capability (DOC, SOP reference 2D0900129) and Proficiency Testing Samples (PT’s, SOP reference 2D0900119);
   4) measures to evaluate detection limits, such as method detection limits (MDL, SOP reference: 2D0900109);
   5) selection of appropriate formulas to reduce raw data to final results such as regression

analysis, comparison to internal/external standard calculations, and statistical analyses;
6) measures to assure the accuracy of the analytical method including Initial and Continuing Calibration Blanks (ICB/CCB), Initial and Continuing Calibration Verifications (ICV/CCV), use of certified reference materials, performance evaluation samples (essential);
7) measures to assure clean glassware and the selection and use of reagents and standards of appropriate quality;
8) use of appropriate techniques to obtain representative subsamples (SOP reference: 2D0900125).

b) The quality control protocols specified by the published test method and/or Standard Operating Procedure will be followed. Where no regulatory quality control protocols are specified FGL will implement those controls which are applicable to the type of sample preparation and analysis being performed (SOP reference: 2D0900110).

c) All quality control measures are assessed and evaluated on an on-going basis. FGL maintains procedures for the development of acceptance/rejection criteria where no method or regulatory criteria exist (SOP reference: 2D0900110);

6.4 Data Validation

In order to determine the validity of data generated the quality controls listed above are reviewed for acceptance. To the extent possible, samples are reported only if all quality control measures are acceptable. If a "critical to data defensibility" quality control measure is found to be out of control, and the data is to be reported, all samples associated with the failed quality control measure are reported with client approval and the appropriate data qualifier(s).

Calculations and data/information entry and transfers are reviewed at the following five specific points:

a) After sample login to verify analyses requested match those analyses which are to be performed. Sampling information such as sample identification, sampling dates and time are also reviewed for transcription accuracy (SOP reference: 2D0900114).
b) After analysis to verify that the quality controls used for analysis and preparation were properly used and valid. Procedures have been defined to properly handle invalid data (SOP reference: 2D0900113). At this time the LIMS performs comprehensive data reviews and reports including:
   1) all calibration criteria are acceptable including a summary report;
   2) all analytical and preparatory quality controls have been performed in the required frequencies including a summary report;
   3) all quality control objectives including a summary report for each type of quality control, such as continuing calibration blanks, continuing calibration verifications, internal standards, method blanks, laboratory control samples and matrix spikes. (Note: method blanks will be investigated if blank contamination exceed the established reporting limit for the associated method. Method blank contamination above reporting limits will require immediate corrective action).
   4) all standards used are NIST traceable and are within expiration (included in the frequency report);
c) After data review the analytical results are reviewed for completeness (SOP reference:2D0900115) by a second analyst or manager. This review is primarily for failures and data integrity. The LIMS generates a summary indicating what failures occurred and any changes which were made to the data.
d) Prior to reporting to verify that data is historically reasonable and appropriate cross checks such as general mineral balances and COD is greater than BOD (SOP reference: 2D0900116).

e) Prior to final signature to verify that the report package is complete in that all analyses requested are being reported and in the proper fashion such as nitrate versus nitrate nitrogen. (SOP reference: 2D0900117).

6.4.1 Calculations used in Data Validation

a) Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator. Accuracy is usually expressed by FGL as percent recovery.
b) Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed by FGL as percent relative standard deviation or relative percent difference.
c) Completeness: the degree to which results are deemed to be valid relative to the total number of results reported. Completeness is usually expressed by FGL as the percentage of valid results. FGL does not normally perform this function but can report this calculation if a project requires.
d) Representativeness: the degree to which results are representative of the site which was sampled. FGL takes steps, such as sample homogenizing and appropriate quantities used for sub-sampling etc., to ensure that the results are relevant and applicable to a specific site/project. However, this is highly dependent on field activities which are out of control of the laboratory. Objectives for representativeness must be determined at the beginning of a project and included in the Field Sampling Plan and Quality Assurance Project Plan.

Table 6.1 Summary list of Quality Controls used by FGL

Quality Control ID	Full Name	Requirement
Analysis QC		
Tune	Instrument Tune	Critical to Data Defensibility
InStd	Internal Standard	Critical to Data Defensibility
CALS	Instrument Calibration	Critical to Data Defensibility
InstB	Instrument Blank	Critical to Data Defensibility
ICV	Initial Calibration Verification	Critical to Data Defensibility

Quality Control ID	Full Name	Requirement
ICB	Initial Calibration Blank	Critical to Data Defensibility
HiStd	Calibration Hi Standard	Critical to Data Defensibility
ICSA	Interference Check Sample A	Critical to Data Defensibility
ICSAB	Interference Check Sample AB	Critical to Data Defensibility
CCV	Continuing Calibration Verification	Critical to Data Defensibility
CCB	Continuing Calibration Blank	Critical to Data Defensibility
IDL	Instrument Detection Limit	Critical to Data Defensibility
LDR	Linear Dynamic Range	Critical to Data Defensibility
RTWin	Retention Time Window	Critical to Data Defensibility
Matrix QC		
PDS	Post Digestion Spike (ICP/GFAA)	Information Only
SDil	Serial Dilution (ICP)	Information Only
Preparation QC		
Surr	Surrogate	Information Only
MDL	Method Detection Limit	Critical to Data Defensibility
Blank	Method Blank	Information Only
LCS	Laboratory Control Standard/Sample	Critical to Data Defensibility
MS	Matrix Spike of MS/MSD pair	Information Only
MSD	Matrix Spike Duplicate of MS/MSD pair	Information Only
BS	Blank Spike of BS/BSD pair	Information Only
BSD	Blank Spike Duplicate of BS/BSD pair	Information Only
Dup	Duplicate Sample	Information Only
ExBlk	TCLP/STLC Extraction Blank	Critical to Data Defensibility
ExDup	TCLP/STLC Extraction Duplicate	Critical to Data Defensibility
SRC	Sample Replicate Check	Information Only

7.0 EQUIPMENT AND REFERENCE MATERIALS

This is primarily referenced from 22 CCR 64815 (b)

7.1 General Requirements

a) The laboratory is furnished with all items of equipment including reference materials, such as certified balance weights and reference thermometers, required for the correct performance of tests for which it is accredited.

b) Each major item of equipment is identified by the serial number, LIMS ID, and inventory control number.

c) Records will be maintained in FGL LIMS of each major item of equipment and all reference materials significant to the tests performed. This list can be made available upon request. The records will include:
1) the name of the item of equipment;
2) the manufacturer's name, type identification, and serial number or other unique identification;
3) date received and date placed in service (if available);
4) current location, where appropriate.

d) Table 7.1 contains a summary listing of equipment including which lab the equipment is located in, the division in which it is used, the quantity, and instrument type. A more detailed listing including information such as specific manufacturers, model numbers will be made available upon request.

7.2 Equipment Maintenance

a) All equipment is routinely maintained, inspected and cleaned. Specific routine maintenance procedures are documented in section 15.0 of each analytical SOP.

b) Any item of equipment which has been subjected to overloading or mishandling, or which gives suspect results, or has been shown by verification or otherwise to be defective, will be clearly identified and taken out of service until it has been repaired and shown by calibration, verification or test to perform satisfactorily (SOP reference:2D0900121). The laboratory will review the effect of this defect on previous analyses.

c) Records will be maintained for all routine and non-routine maintenance performed. These procedures are outlined in the instrument maintenance SOP (SOP reference:2D0900121). Records of the maintenance will include:
1) the manufacturer's name, model number, serial number and instrument identification;
2) the date the maintenance was performed and the analyst or service technician who performed the maintenance;
3) the symptoms of problems occurring on the instrument;
4) the cause of the problems occurring on the instrument;
5) the repair/maintenance performed to correct the problem.

7.3 Reference Equipment

a) Reference equipment of measurement held by the laboratory (such as calibrated weights or thermometers) shall be used for calibration only and for no other purpose. Reference equipment of measurement are calibrated by a body that can provide NIST or other appropriate national standards of measurement traceability.

b) FGL maintains a program for calibration and verification for reference equipment (SOP

reference 2D0900121). Please refer to section 9.3.2 for information regarding use of reference equipment and calibration of the support equipment such as thermometers, balances and mechanical pipets.

Table 7.1 Summary list of equipment

LAB	DIVISION	QUANTITY	INSTRUMENT TYPE
Santa Paula	Organic	6	Gas Chromatograph/Mass Spectrometer
Santa Paula	Organic	8	Gas Chromatograph
Santa Paula	Organic	1	High Performance Liquid Chromatograph
Santa Paula	Organic	4	Purge and Trap Systems
Santa Paula	Organic	1	Total Organic Carbon Analyzer
Santa Paula	Organic	2	Analytical Balance
Santa Paula	Organic	1	Gas/Liquid Chromatograph MS/MS
Santa Paula	Inorganic	2	Inductively Coupled Plasma/Mass Spectrometer
Santa Paula	Inorganic	1	Inductively Coupled Plasma Spectrophotometer
Santa Paula	Inorganic	1	Automated Mercury Analyzer
Santa Paula	Inorganic	3	Ion Chromatograph with autosampler
Santa Paula	Inorganic	1	Flow injection autoanalyzer
Santa Paula	Inorganic	3	UV/VIS Spectrophotometer
Santa Paula	Inorganic	2	Nephelometer
Santa Paula	Inorganic	1	Oxygen Meter
Santa Paula	Inorganic	1	Conductivity Meter
Santa Paula	Inorganic	2	pH Meter
Santa Paula	Inorganic	1	Setaflash
Santa Paula	Inorganic	3	Analytical Balance
Santa Paula	Radio	1	Alpha Scintillation
Santa Paula	Radio	1	Liquid Scintillation
Santa Paula	Radio	8	Alpha Counter
Santa Paula	Radio	3	Alpha/Beta Counter
Santa Paula	Radio	2	Balance
Santa Paula	Agronomics	5	Inductively Coupled Plasma Spectrophotometer
Santa Paula	Agronomics	2	UV/VIS Spectrophotometer
Santa Paula	Agronomics	1	pH Meter
Santa Paula	Agronomics	2	EC Meter
Santa Paula	Agronomics	1	Chloridometer
Santa Paula	Agronomics	1	Nitrogen Analyzer
Santa Paula	Agronomics	2	Carbon/Nitrogen/Sulfur Analyzer
Santa Paula	Agronomics	6	Analytical Balance
Santa Paula	Bacti	6	Incubators
Santa Paula	Bacti	3	Waterbaths
Santa Paula	Bacti	2	Autoclaves
Santa Paula	Field Service	9	Vehicles

LAB	DIVISION	QUANTITY	INSTRUMENT TYPE
Santa Paula	Field Service	10	Isco Autosamplers
Stockton	Laboratory	2	Refrigerator
Stockton	Inorganic	1	UV/VIS Spectrophotometer
Stockton	Inorganic	1	Nephelometer
Stockton	Inorganic	2	Oxygen Meter
Stockton	Inorganic	1	pH Meter
Stockton	Inorganic	1	Conductivity Meter
Stockton	Inorganic	3	Analytical Balance
Stockton	Inorganic	3	Incubators -BOD Analysis
Stockton	Inorganic	2	Oven
Stockton	Bacti	4	Incubators -Micro
Stockton	Bacti	4	Waterbaths
Stockton	Bacti	2	Autoclaves
Stockton	Field Service	5	Vehicles
Stockton	Field Service	17	Isco Autosamplers
Chico	Laboratory	2	Refrigerator
Chico	Inorganic	1	UV/VIS Spectrophotometer
Chico	Inorganic	1	Nephelometer
Chico	Inorganic	1	Oxygen Meter
Chico	Inorganic	1	pH/ISE Meter
Chico	Inorganic	1	Analytical Balance
Chico	Bacti	3	Incubators
Chico	Bacti	2	Waterbaths
Chico	Bacti	2	Autoclaves
Chico	Field Service	3	Vehicles
SLO	Laboratory	1	Refrigerator
SLO	Inorganic	1	pH Meter
SLO	Bacti	1	Analytical Balance
SLO	Bacti	6	Incubators
SLO	Bacti	3	Waterbaths
SLO	Bacti	2	Autoclaves
SLO	Field Service	2	Vehicles
Visalia	Laboratory	2	Refrigerator
Visalia	Inorganic	1	pH Meter
Visalia	Bacti	1	Analytical Balance
Visalia	Bacti	3	Incubators
Visalia	Bacti	2	Waterbaths
Visalia	Bacti	1	Autoclaves
Visalia	Field Service	2	Vehicles

8.0 MEASUREMENT TRACEABILITY AND CALIBRATION

This is primarily referenced from 22 CCR 64815 (b)

8.1 General Requirements

All measuring operations and testing equipment having an effect on the accuracy or validity of tests are calibrated and/or verified before being put into service and on a continuing basis. FGL maintains a program for the calibration and verification of its measuring and test equipment. This includes balances, thermometers and control standards.

8.2 Traceability of Calibration

The overall program of calibration and/or verification and validation of equipment has been designed and operated so as to ensure that, wherever applicable, measurements made by the laboratory are traceable to NIST or other appropriate national standards of measurement. All standards are documented at the laboratory for future traceability (SOP reference:2D0900104).

8.2.1 Documentation and Labeling of Standards

Documented procedures are maintained for the purchase, reception and storage of calibration standards used for the technical operations of the laboratory.

a) The laboratory retains records for all standards including the manufacturer/vendor, the manufacturer's Certificate of Analysis or purity (if supplied), the date of receipt, recommended storage conditions, and an expiration date after which the standard will not be used unless it is verified by the laboratory.
b) The original stock standard containers (such as provided by the manufacturer or vendor) are labeled with an expiration date.
c) Detailed records are maintained for standard preparation. These records indicate traceability to purchased stocks or neat compounds, reference to the method of preparation, date of preparation, expiration date and preparer's initials.
d) All containers of stock and prepared standards bear a unique identifier and expiration date and are linked to the documentation listed in 9.2.1 a) above.

8.3 Calibration

8.3.1 General Requirements

a) Each calibration is dated and labeled with the test method, instrument, analysis date, and each analyte name, concentration and response (or response factor).
b) Sufficient information is recorded to permit reconstruction of the calibration.
c) Criteria for the acceptance of a calibration procedure, such as calibration curves and concentration (titer) determinations of titrants, are established. General criteria are listed below. Detailed criteria are listed in section 11.0 of each analytical SOP.

8.3.2 Reference Equipment Calibrations

This equipment includes thermometers, balances, balance weights and radiation survey meters . All reference equipment is:

a) Maintained in proper working order. The records of all calibrations are retained.

b) Calibrated using NIST traceable references when available, over the entire range of use. The results of such calibration shall be within the specifications required of the application for which is equipment is used or:
   1) The equipment shall be removed from service until repaired; or
   2) FGL will prepare a deviation curve and correct all measurements for the deviation. All measurements will be recorded and maintained.

c) Calibrated according to the following frequencies:
   1) The primary NIST traceable reference thermometer is calibrated by an outside source on an annual basis. Secondary thermometers used for verification of ovens, refrigerators, freezers, incubators and water baths shall be calibrated with the primary NIST traceable reference on an annual basis. Thermometers used for microbiological procedures are calibrated with the primary NIST traceable reference on a semi-annual basis. The temperature correction is posted on the thermometer (SOP reference:2D0900118).
   2) Balances and balance verification weights are calibrated with NIST traceable references on an annual basis (SOP reference:2D0900123).

8.3.3 Support Equipment Calibration Verifications

This equipment includes balances, volumetric dispensing devices (such as Eppendorf®, or automatic dilutor/dispensing devices), autoclaves and ovens, refrigerators, freezers, incubators, water baths. Calibration verification of volumetric dispensing devices is performed if quantitative results are dependent on their accuracy, as in standard preparation and dispensing or dilution into a specified volume. All support equipment is:

a) Maintained in proper working order. The records of all activities including service calls are retained.
b) Verified using NIST traceable references when available. The results of the verification shall be within the specifications required of the application for which is equipment is used or the equipment shall be removed from service until repaired.
c) Verifications according to the following frequencies:
   1) Ovens, refrigerators, freezers, incubators and water baths shall be verified with NIST traceable references prior to use on each working day. Additional monitoring as prescribed by the test method shall be performed for any device that is used in a critical test (such as incubators or water baths). The acceptability for use or continued use shall be according to the needs of the analysis or application for which the equipment is being used (SOP reference:2D0900118).
   2) Balances are verified with NIST traceable references prior to use on each working day (SOP reference:2D0900123).
   3) Volumetric dispensing devices (except Class A glassware) are verified for accuracy and precision on a quarterly basis (SOP reference:2D0900124).
   4) Autoclave sterilization temperatures and pressures for each run are documented by the use of spore strips.

8.3.4 Instrument Calibrations

a) Calibration curves are prepared as specified in the published test method. If the published test method does not provide guidance in the preparation of a calibration curve (e.g. number of calibration points and range), FGL will use a minimum of two standards plus a zero reference standard.

b) The calibration curve is subjected to a calibration linearity test, such as a linear regression or percent RSD of response factors (internal standard calibration) or calibration factors

(external standard calibration). For those methods which do not contain specific acceptance criteria FGL applies the following:

1) Organics: if, spanning the range of calibration, the RSD of response factors is less than 15 percent, or the RSD of calibration factors is less than 30 percent, an average relative response factor may be used. If that fails then a linear least squares fit is used with a weighted coefficient of determination no less than 0.99. If that fails then a quadratic least squares fit is used with weighted coefficient of determination no less than 0.99.
2) Inorganics: a linear regression or quadratic may be used with a correlation coefficient no less than 0.995.

c) Prior to specific analyte calibrations certain tests may require an instrument calibration such as a GC/MS or ICP/MS tune. Acceptance criteria are normally defined in the published test method and must be met prior to instrument use. These criteria are also listed in the specific SOP for that instrument.

8.3.5 Calibration Verification

8.3.5.1 Initial Calibration Verification (ICV) and Blank (ICB)

a) When available, all initial calibrations are verified with a matrix matched blank (ICB) and a standard obtained from a second or different source(ICV). The ICB and ICV are analyzed with each initial calibration and must be within acceptance range specified by the published test method or limits statistically derived by FGL.
b) If the initial calibration verification fails, the analysis procedure will be stopped and evaluated. For example, a second standard may be analyzed and evaluated or a new initial calibration curve may be established and verified. In all cases, the initial calibration verification will be acceptable before analyzing any samples.

8.3.5.2 Continuing Calibration Verification (CCV) and Blank (CCB)

Additional standards are analyzed after the initial calibration curve or the integrity of the initial calibration curve (see 9.3.4.1 above) has been accepted.

a) These standards are analyzed at a frequency specified by the published test method. If published frequencies are not available a minimum frequency of 5% or every 12 hours whichever is more frequent will be used. The verification may use the standards from the original calibration curve or standards from another source.
b) When an initial calibration curve is not established on the day of analysis, the integrity of the initial calibration curve is verified on each day of use (or 24 hour period) by initially analyzing an CCB and CCV at the method defined concentration or a mid-level concentration if not included in the test method.
c) If a calibration check standard fails, and routine corrective action procedures fail to produce a second consecutive calibration check within acceptance criteria, a new initial calibration curve is performed. When the continuing calibration verification acceptance criteria are exceeded high (i.e., high bias) on an automated analytical run, and there are non-detects for the corresponding analyte in environmental samples associated with the continuing calibration check, then those non-detects may be reported. Positive samples affected by the unacceptable check are reanalyzed after a new calibration curve has been established, evaluated and accepted. Additional automated sample analysis will not occur until a new calibration curve is established and verified. Non-automated analyses are corrected by recalibration at the time of analysis.

9.0 TEST METHODS

This is primarily referenced from 22 CCR 64815 (b)

9.1 Test Methods Documentation

FGL maintains published test methods and standard operating procedures which provide a reference for and specific instructions on the use and operation of all relevant equipment, handling and preparation of samples, calibration and/or testing and administrative procedures. All instructions, standards, manuals and reference data relevant to the work of the laboratory will be maintained up-to-date and be readily available to the staff. The list of all test methods accredited and/or performed by FGL are available on-line.

9.1.1 Published Test Methods

a) The laboratory maintains a collection of current published test method manuals for each accredited analyte or test method. The list of method references which FGL uses is listed in section 16.0 of this document.
b) Copies of all published test methods are accessible to all personnel.
c) A comprehensive list of all methods which FGL is capable of performing is available.

9.1.2 Standard Operating Procedures (SOP)

FGL maintains internally written standard operating procedures that accurately reflect all phases of current laboratory activities such as assessing data integrity, corrective actions, performance evaluation study handling, and all test methods. FGL utilizes two standard SOP formats, analytical/preparation and administrative (SOP references:2D0900043 and 2D0900101 respectively).

a) Copies of all SOPs are accessible to all personnel.
b) The SOPs are organized by the location (e.g. department or customer) in which they are used. SOP's which are used by many locations are controlled to each applicable location (SOP reference: 2D0900111).
c) Each SOP clearly indicates the effective date of the document, the revision number and the signature(s) of the approving authorities.
d) The SOPs are reviewed and updated every two years or more often if method updates or changes is warranted.

9.2 Method Certification

Prior to being accredited for a test method FGL will perform an initial demonstration of capability. This process is used to verify that the procedure is accurate, precise and meets all published regulatory criteria where applicable. Upon demonstrating acceptable results FGL will maintain the records and provide a report package to the appropriate regulatory agency to obtain certification.

9.2.1 Demonstration of Capability

a) Prior to the use of any test method, each analyst must provide a demonstration of capability. The following demonstration of capability requirements are based on EPA test method section for Initial Demonstration of Capabilities and 40 CFR 136.7.
    1) A quality control sample will be obtained from an outside source. If not available, the QC check sample may be prepared by the laboratory using stock standards that are

prepared independently from those used in instrument calibration.

2) The concentrate will be diluted in a volume of clean matrix sufficient to prepare four aliquots at the required method volume to a concentration approximately 10 times the method-stated or laboratory-calculated method detection limit.
3) The four aliquots shall be prepared and analyzed according to the test method either concurrently or over a period of days.
4) Using the four results, calculate the average recovery in the appropriate reporting units (such as ug/L) and the standard deviation of the population sample (in the same units) for each parameter of interest.
5) For each parameter, compare the standard deviation and average to the corresponding acceptance criteria for precision and accuracy in the test method (if applicable) or in laboratory-generated acceptance criteria (if a non-standard method). If the standard deviation and average for all parameters meet the acceptance criteria, the method will be considered acceptable and the certification process may continue. If any one of the parameters exceed the acceptance range, the performance is unacceptable for that parameter.
6) When one or more of the tested parameters fail at least one of the acceptance criteria, the analyst must proceed according to a) or b) below.
    i) Locate and correct the source of the problem and repeat the test for all parameters of interest beginning with 3) above.
    ii) Beginning with 3) above, repeat the test for all parameters that failed to meet criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with 3).

c) Thereafter, continuing demonstration of method performance (such as laboratory control samples) is required.
d) In all cases, the appropriate documentation is completed and retained by the laboratory to be made available upon request. All associated supporting data necessary to reproduce the analytical results is retained by the laboratory.

9.3 Agency Certification or Approval

Prior to performing a test method in a given region, FGL will obtain the necessary agency certification. Below is a list of all agencies for which FGL has been certified or approved for analysis (all certifications are available upon request):

a) All FGL laboratories maintain certifications or approval for the following agencies:

i. California - Department of Public Health

10.0 SAMPLE HANDLING

This is primarily referenced from 22 CCR 64815 (b).

10.1 Sample Tracking

a) The laboratory maintains a documented system for uniquely identifying the samples to be tested, to ensure that there can be no confusion regarding the identity of sample at any time (SOP Reference:2D0900146). This system includes identification for all samples, subsamples and carried forward to subsequent extracts and/or digestates. The laboratory assigns a unique identification (ID) code to each sample container received in the laboratory.
b) This laboratory ID code will maintain an unequivocal link with the unique field ID code assigned each container.
c) The laboratory ID code is placed on the sample container as a durable label.
d) The laboratory ID code is entered into the LIMS and is the link that associates the sample with related laboratory activities such as sample preparation or analysis.

10.2 Sample Acceptance

The laboratory maintains a written sample acceptance criteria that clearly outlines the circumstances under which samples will be accepted (SOP reference:2D0900146). This SOP is available to sample collection personnel and includes, but is not limited to, the following areas of concern:

a) Proper, full, and complete documentation, which includes sample identification, the location, date and time of collection, collector's name, container type, preservation type, sample type and any special remarks concerning the sample. FGL maintains documented procedures listing proper containers and preservation (*Sample Container and Preservation Guidelines***,** Form reference: 2D0900138);
b) Proper sample labeling to include unique identification and a labeling system for the samples with requirements concerning the durability of the labels (water resistant) and the use of indelible ink;
d) Adherence to specified holding times;
e) Adequate sample volume. Sufficient sample volume must be available to perform the necessary tests; and
f) Procedures to be used when samples which show signs of damage or contamination.

10.3 Sample Receipt Protocols

a) Upon receipt, the condition of the sample, including any abnormalities or departures from standard condition as prescribed in the relevant test method, are recorded.
   1) All samples which require thermal preservation are considered acceptable if the arrival temperature is either within +/-2^{o}C of the required temperature or the method specified range. For samples with a specified temperature of 4^{o}C, samples with a temperature ranging from just above the freezing temperature of water to 6^{o}C shall be acceptable. Samples that are hand delivered to the laboratory immediately after collection may not meet this criteria.
   In these cases, the samples will be considered acceptable if there is evidence that the chilling process has begun such as arrival on ice.
   2) FGL has documented procedures for checking chemical preservation such as pH at the time of sample receipt.
b) The results of all checks are recorded.

c) Where there is any doubt as to the item's suitability for testing, where the sample does not conform to the description provided, or where the test required is not fully specified, FGL will consult the client for further instruction before proceeding. If the sample does not meet the sample receipt acceptance criteria FGL will either:
   1) Retain correspondence and/or records of conversations concerning the final disposition of rejected samples; or
   2) Fully document any decision to proceed with the analysis of samples not meeting acceptance criteria.
      i) The condition of these samples will be noted on the chain of custody or sample discrepancy form;
      ii) The analysis data will be appropriately "qualified" on the final report.

d) FGL utilizes a LIMS electronic database to document receipt of all sample containers.
   1) At a minimum, the following is recorded in the LIMS:
      i) Client Name and Address
      ii) Project Name
      iii) Sample description
      iv) Sample date and time
      v) Name of sampler and employer
      vi) Date and time of laboratory receipt
      vii) Name of person who received the sample
      viii) Unique laboratory ID code
      ix) Analytical test methods requested
      x) Container types and preservation
      xi) Initials of person making the entries.

e) All documentation, such as a fax transmittal form, that is transmitted either by FGL or by the sample transmitter will be retained.

f) A complete chain of custody record is retained.

10.4 Storage Conditions

The laboratory maintains documented procedures and appropriate facilities to avoid deterioration, contamination, or damage to the sample during storage, handling, preparation, and testing; any relevant instructions provided with the sample will be followed (2D0900146). Where items have to be stored under specific environmental conditions, these conditions will be maintained, monitored and recorded where necessary.

a) Samples are stored according to the conditions specified by preservation protocols:
   1) Samples which require thermal preservation shall be stored under refrigeration which is +/-2^{o}C of the specified preservation temperature unless method specific criteria exist. For samples with a specified storage temperature of 4^{o}C, storage at a temperature above the freezing point of water to 6^{o}C shall be acceptable.
   2) Samples, sample fractions, extracts, leachates and other sample preparation products are stored away from all standards, reagents, food and other potentially contaminating sources. Samples shall be stored in such a manner to prevent cross contamination.

10.5 Sample Disposal

The laboratory maintains a Hazardous Waste Management Plan which outlines procedures for the disposal of samples, digestates, leachates and extracts or other sample preparation products. Information is also included in section 16.0 of each analytical SOP.

10.6 Sample Subcontracting

a) FGL will advise the client of its intention to sub-contract any portion of the testing to another party.
b) When work is subcontracted, it is done so under chain of custody, and the proper records are included with the report package. When work is subcontracted to an outside laboratory a separate chain of custody is prepared.
c) When subcontracted work is reported by FGL a cover letter is supplied indicating the laboratory which performed the analysis. All original reports and chain of custodies resulting from the subcontracted work are provided to the client.
d) Subcontractors are reviewed for acceptability based on an evaluation of their Quality Manual and reporting format (SOP reference:2D0900107). On-site audits may be performed based on project specific requirements.

11.0 RECORDS

FGL maintains a record system to comply with all relevant regulations. The system can produce unequivocal, accurate records which document all laboratory activities. FGL retains on record all original observations, calculations and derived data, calibration records and a copy of the test report. This is primarily referenced from 22 CCR 64815 (b)

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11.1 Record Keeping System and Design

The record keeping system allows historical reconstruction of all laboratory activities that produced the resultant sample analytical data. This includes interlaboratory transfers of samples and/or extracts.

a) The records include the identity of personnel involved in sampling, preparation, calibration or testing.
b) The records include all information relating to the laboratory facilities equipment, analytical test methods, and related laboratory activities, such as sample receipt, sample preparation, or data verification.
c) The record keeping system facilitates, the retrieval of all working files and archived records for inspection and verification purposes.
d) All documentation entries are signed or initialed by responsible staff. The reason for the signature or initials is clearly indicated in the records such as “sampled by”, “prepared by”, or “reviewed by”).
e) All generated data except those that are generated by automated data collection systems, are recorded directly, promptly and legibly in permanent ink.
f) Entries in records are not obliterated by methods such as erasures, overwritten files or markings. All corrections to record-keeping errors shall be made by one line marked through the error. The individual making the correction shall sign (or initial) and date the correction. These criteria also apply to electronically maintained records.

11.2 Hardcopy Records Management and Storage

a) All records (including those pertaining to calibration and test equipment), certificates and reports are safely stored, held secure and in confidence to the client (SOP reference:2D0900160).
b) All client records are held in strict confidence and will not be provided to any other party without consent of the client (SOP reference:2D0900099).
c) All records, including those specified in 12.4, are retained for a minimum of five years. All information necessary for the historical reconstruction of data is maintained by the laboratory. Records which are stored only on electronic media are supported by the hardware and software necessary for their retrieval.
d) The laboratory has established a record management system for control of laboratory notebooks (SOP reference:2D0900103). Information which is part of a routine analysis is considered to be a record (such as run schedules). Controlled logbooks are typically used for quality assurance documentation such as daily balance, temperature, conductivity checks and instrument maintenance and personal analyst logbooks.
e) Access to archived information is documented with an access log. These records are protected against fire, theft, loss, environmental deterioration, vermin and, in the case of electronic records, electronic or magnetic sources.

11.3 Electronic Records Management and Storage

Where computers or automated equipment are used for the capture, processing, manipulation,

recording, reporting, storage or retrieval of test data, the laboratory ensures that:

a) computer software is documented and adequate for use;
b) computer and automated equipment are maintained to ensure proper functioning and provided with the environmental and operating conditions necessary to maintain the integrity of calibration and test data;
c) Records that are stored or generated by computers or personal computers (PC's) have hard copy or write-protected backup copies.
d) Records which are stored only on electronic media are supported by the hardware and software necessary for their retrieval.
e) procedures are established for protecting the integrity of data; these procedures include data entry or capture, data storage, data transmission and data processing, maintenance of security of data includes the prevention of unauthorized access to, and the unauthorized amendment of, computer records.
f) procedures are established for protecting existing data through backing up the appropriate electronic data storage areas (2D0900198)

11.4 Sample Handling Records

A record of all procedures to which a sample is subjected while in the possession of the laboratory are maintained. These include records pertaining to:

a) Sample preservation including appropriateness of sample container and compliance with holding time requirement;
b) Sample identification, receipt, acceptance or rejection and log-in;
c) Sample storage and tracking including shipping receipts, transmittal forms;
d) Sample preparation including cleanup and separation protocols, ID codes, volumes, weights;
e) Sample analysis including all original raw data, whether hard copy or electronic, for calibrations, samples and quality control measures, including analysts work sheets and data output records (chromatograms, strip charts, and other instrument response readout records); these records will include the following:
    1) Laboratory sample ID code;
    2) Date of analysis;
    3) Instrumentation identification and instrument operating conditions/parameters (or reference to such data);
    4) Analysis type;
    5) All manual calculations; and
    6) Analyst's or operator's initials
    7) Reviewers initials
f) Standard origin, receipt, preparation, and use;
g) Equipment receipt, use, specification, operating conditions and preventative maintenance;
h) Calibration criteria, frequency and acceptance criteria;
i) Data and statistical calculations, review, confirmation, interpretation, assessment and reporting conventions;
j) Method performance criteria including expected quality control requirements;
k) Quality control protocols and assessment;
l) Electronic data security, software documentation and verification, software and hardware audits, backups, and records of any changes to automated data entries;

11.5 Laboratory Support Activities

In addition to documenting all the above-mentioned activities, the following shall be retained:
a) Copies of final reports;

b) Archived standard operating procedures;
c) Correspondence relating to laboratory activities for a specific project;
d) All corrective action reports, audits and audit responses;
e) Proficiency test results and raw data; and
f) Personnel qualifications, experience and training records;
g) Initial and continuing demonstration of proficiency for each analyst; and
h) A log of names, initials and signatures for all individuals who are responsible for signing or initialing any laboratory record.

12.0 LABORATORY REPORT FORMAT AND CONTENTS

This is primarily referenced from 22 CCR 64815 (b)

The results of each test, or series of tests carried out by FGL are reported accurately, clearly, unambiguously and objectively. The results are provided in a test report and include all the information necessary for the interpretation of the test results and all information required by the method used. Some regulatory reporting requirements or formats such as the California drinking water Write-on format, may not require all items listed below, however, FGL will provide all the required information in the proper format to the client to meet the requirements of such regulatory reports.

a) Unless client or regulatory agencies require otherwise, each report to a client shall include at least the following information:
   1) A title indicating analytical results;
   2) FGL laboratory addresses and the laboratory certification number;
   3) Laboratory ID number linking the report information to all analytical, custody and field documentation. This includes identification on each page and total number of pages.
   4) Name and address of client, and project name if applicable;
   5) Description of the tested sample;
   6) Date of receipt of sample, date and time of sample collection, date(s) of preparation and analysis performed. For microbiology reports, the time of preparation and analysis is listed;
   7) Identification of results derived from samples that did not meet acceptance requirements such as improper container, holding time or temperature;
   8) Identification of the test method used;
   9) If FGL performed the sampling, a reference to the method used;
   10) Any deviations from the test method including data qualifiers and there meaning;
   11) Testing results including supporting information such as reporting units or reporting on dry weight basis;
   12) When appropriate, a statement of the estimated uncertainty of the test result;
   13) A signature and title, or an equivalent electronic identification of the person(s) accepting responsibility for the content of the report, and date of issue;

b) FGL provides many custom options for laboratory sample data and quality assurance reports. This includes Drinking Water Summaries, Irrigation Water Interpretations as well as electronic deliverables such as SWAMP EDI and Geotracker formats.

c) Where the report package contains results of tests performed by sub-contractors, these results are clearly identified with a cover letter and the original full subcontractor report and supporting custody records.

d) After issuing the report, it may be necessary to amend the original report. In this regard the appropriate sections of the report being amended will be indicated in the Case Narrative section of the report (SOP reference:2D0900092). If an electronic deliverable was provided the electronic deliverable will be amended and redelivered.

e) FGL will notify clients promptly of any event such as the identification of defective measuring or test equipment that casts doubt on the validity of results given in any report package or amendment to a report package.

f) Where clients require transmission of test results by telephone, fax or other electronic or electromagnetic means, staff will follow documented procedures that ensure confidentiality.

13.0 OUTSIDE SUPPORT SERVICES AND SUPPLIES

This is primarily referenced from 22 CCR 64815 (b)

13.1 Subcontracted Analyses

FGL will subcontract all regulatory testing to NELAP accredited laboratories whenever possible. When this is not possible the analytical subcontractors used by FGL will be evaluated. The evaluation is performed by review of the Quality Assurance Plan and reports applicable to the test being subcontracted (SOP reference:2D0900107). On-Site audits of subcontractors are performed only if it is a project specific requirement. All subcontractor report packages will be clearly identified with a cover letter and the original full subcontractor report and supporting custody records.

If there are any indications that a subcontractor has knowingly supplied services of substandard quality, this information will be forwarded to all clients impacted.

13.2 Laboratory Supplies

a) Upon receipt of supplies FGL receiving/shipping personnel will verify the content of the supplies against the packing slip SOP reference:2D1000050). If the shipment is complete and the supplies received are in acceptable condition then they are provided to the department which placed the order and the approved packing slip is provided to accounting. If the shipment is incomplete or the supplies are unacceptable then the FGL department and the vendor are notified. Arrangements are then made with the vendor to complete the order or obtain supplies in acceptable condition.
b) Containers, chemicals and standards are recorded in LIMS.
c) Wherever possible analytical reagent grade chemicals and NIST traceable standards are purchased. These supplies are considered acceptable for use by meeting the positive and negative quality control objectives of the analytical test being performed.

13.3 Laboratory Equipment

FGL will, wherever possible or relevant, ensure that purchased equipment is not used until it has been inspected, calibrated or otherwise verified as complying with any standard specifications relevant to the calibrations or tests concerned.

13.4 Laboratory Water Quality

The reagent water utilized by the laboratories meet the criteria listed in SM 1080 C, Table 1080II: *Reagent Water Specifications* and SM 9020 Table II for *Quality of Reagent Water Used in Microbiology Testing*

a) Daily
   1) Conductivity, criteria is less than 1 μmhos/cm at 25°
b) Monthly water checks
   1) HPC, criteria < 500/mL (pour plate method)
   2) TOC, criteria <1 mg/L
   3) Total Chlorine, criteria <0.01 mg/L (DPD method)
   4) Ammonia/Organic Nitrogen, criteria <0.1 mg/L

c) Annually
1) Heavy metals, single (Cd, Cr, Cu, Ni, Pb and Zn), criteria <0.05 mg/L
2) Heavy metals, total, criteria <0.1 mg/L
3) Bacteriological quality of reagent water, criteria: ratio 0.8 to 3.0

14.0 COMPLAINTS

When a complaint, or other circumstance, raises doubt concerning FGL's compliance with internal policies or procedures, or with external regulatory or client specified requirements, FGL will perform the following steps:

a) Promptly review or audit those areas of activity and responsibility;

b) Upon completion of the review, appropriate steps will be taken to correct the complaint and;

c) Where relevant, the practices which led to the complaint will be corrected.

d) Records of the complaint and subsequent actions will be maintained though the non-conformance/corrective action program (SOP reference:2D0900105) and LIMS Customer Communication program (SOP Reference 2D0900128)

15.0 REFERENCES

15.1 General Reference List

References for this plan include quality assurance, laboratory and field methods published by the U.S. Environmental Protection Agency (EPA) and other agencies mainly through the following sources:

a) "Standard Methods for the Examination of Water and Wastewater," APHA, 20th Edition, 1998.

b) "Standard Methods for the Examination of Water and Wastewater," APHA, 21th Edition, 2005.

c) "Standard Methods for the Examination of Water and Wastewater," APHA, 22th Edition, 2012

d) "Methods for Chemical Analysis in Waters and Waste," (MCAWW) EPA-600/4-79-020

e) "Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater," EPA Method Book, EPA 600/4-82-057, July 1982.

f) "Methods for Evaluating Solid Waste," SW-846, 3rd edition

g)"Prescribed Procedures for Measurement of Radioactivity in Drinking Water," EPA Method Book, EPA-600/4-80-032, August 1980.

h)"Handbook for Sampling and Sample Preservation of Water and Wastewater," EPA Method Book, EPA-600/4-82-029, September 1982.

i)"Eastern Environmental Radiation Facility Radiochemistry Procedures Manual," EPA Method Book, EPA 520/5-84-006, August 1984.

j) "Environmental Measurements Laboratory Procedures," HASL-300, 28th Edition, February 1997 (online at http://www.eml.doe.gov/publications/procman/) .

k) “Environmental Laboratory Sector”, Doc ID EL-V1M1-2011, TNI Standard, July 2011

16.0 DEFINITIONS

Acceptance Criteria: specified limits placed on characteristics of an item, process, or service defined in requirement documents. (ASQC)

Accreditation: the process by which an agency or organization evaluates and recognizes a program of study or an institution as meeting certain predetermined qualifications or standards, thereby accrediting the laboratory.

Accuracy: the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator. (Glossary of Quality Assurance Terms, QAMS, 8/31/92).

Analytical Detection Limit: the smallest amount of an analyte that can be distinguished in a sample by a given measurement procedure throughout a given (e.g., 0.95) confidence interval. (Applicable only to radiochemistry)

Analytical Reagent (AR) Grade: designation for the high purity of certain chemical reagents and solvents given the American Chemical Society. (Quality Systems)

Batch: environmental samples which are prepared and/or analyzed together with the same process and personnel, using the same lot(s) of reagents. A preparation batch is composed of one to 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An analytical batch is composed of prepared environmental samples (extracts, digestates or concentrates) which are analyzed together as a group using the same calibration curve or factor. An analytical batch can include prepared samples originating from various environmental matrices and can exceed 20 samples. (Quality Systems)

Blank: a sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results. (ASQC, Definitions of Environmental Quality Assurance Terms, 1996)

Calibrate: to determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device, or the correct value for each setting of a control knob. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements.

Calibration: the set of operations which establish, under specified conditions, the relationship between values indicated by a measuring instrument or measuring system, or values represented by a material measure, and the corresponding known values of a measurand. (VIM - 6.13)

Calibration Curve: the graphical relationship between the known values, such as concentrations, of a series of calibration standards and their analytical response.

Calibration Standard: a solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The Calibration solutions are used to calibrate the instrument response with respect to analyte concentration. (Glossary of Quality Assurance Terms, QAMS, 8/31/92).

Certified Reference Material (CRM): a reference material one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate or other documentation which is issued by a certifying body. (ISO Guide 30 - 2.2)

Chain of Custody: an unbroken trail of accountability that documents the physical security of samples, data and records.

Confirmation: verification of the presence of a component through the use of an analytical technique that differs from the original test method. These may include: Second column confirmation, Alternate wavelength, Derivatization, Mass spectral interpretation, Alternative detectors or Additional cleanup procedures.

Corrective Action: action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence. (ISO 8402)

Data Audit: a qualitative and quantitative evaluation of the documentation and procedures associated with environmental measurements to verify that the resulting data are of acceptable quality (i.e., that they meet specified acceptance criteria.

Data Reduction: the process of transforming raw data by arithmetic or statistical calculations, standard curves, concentration factors, etc., and collation into a more useful form.

Detection Limit: the lowest concentration or amount of the target analyte that can be determined to be different from zero by a single measurement at a stated degree of confidence. See Method Detection Limit.

Document Control: the act of ensuring that documents (and revisions thereto) are proposed, reviewed for accuracy, approved for release by authorized personnel, distributed properly and controlled to ensure use of the correct version at the location where the prescribed activity is performed. (ASQC, Definitions of Environmental Quality Assurance Terms, 1996)

Duplicate Analyses: the analyses or measurements of the variable of interest performed identically on two subsamples of the same sample. The results from duplicate analyses are used to evaluate analytical or measurement precision but not the precision of sampling, preservation or storage internal to the laboratory.

Environmental Detection Limit (EDL): the smallest level at which a radionuclide in an environmental medium can be unambiguously distinguished for a given confidence interval using a particular combination of sampling and measurement procedures, sample size, analytical detection limit, and processing procedure. The EDL shall be specified for the 0.95 or greater confidence interval. The EDL shall be established initially and verified annually for each test method and sample matrix. (Radioanalysis Subcommittee)

Holding Times (Maximum Allowable Holding Times): the maximum times that samples may be held prior to analysis and still be considered valid. (40 CFR Part 136).

Initial Demonstration of Capability: procedure to establish the ability of the laboratory to generate acceptable accuracy and precision which is included in many of the EPA's analytical test methods. In general the procedure includes the addition of a specified concentration of each analyte (using a QC check sample) in each of four separate aliquots of laboratory pure water. These are carried through the entire analytical procedure and the percentage recovery and the standard deviation are determined and compared to specified limits. (40 CFR Part 136).

Internal Standard: a known amount of standard added to a test portion of a sample and carried through the entire measurement process as a reference for evaluating and controlling the precision and bias of the applied analytical test method.

Laboratory Control Sample (however named, such as laboratory fortified blank or spiked blank): a sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standards or a material containing known and verified amounts of analytes. It is generally used to establish intra-laboratory or analyst specific precision and bias or to assess the performance of all or a portion of the measurement system.

Laboratory Duplicate: Aliquots of a sample taken from the same container under laboratory conditions and processed and analyzed independently.

Limit of Detection (LOD): the lowest concentration level that can be determined by a single analysis and with a defined level of confidence to be statistically different from a blank. (Analytical Chemistry, 55, p.2217, December 1983, modified) See also Method Detection Limit.

Manager (however named): the individual designated as being responsible for the overall operation, all personnel, and the physical plant of the environmental laboratory. A supervisor may report to the manager. In some cases, the supervisor and the manager may be the same individual.

Matrix: The component or substrate which contains the analyte of interest. For purposes of batch determination, the following major matrix types are used at FGL:

> **Aqueous**: Any aqueous sample excluded from the definition of a drinking water matrix or Saline/Estuarine source. Includes surface water, groundwater and effluents.
> **Water**: Any aqueous sample that has been designated a potable or potential potable water source.
> **Liquid**: Any organic liquid with <15% settleable solids.
> **Solids**: Includes soils, sediments, sludges and other matrices with >15% settleable solids.

Matrix Spike (spiked sample, fortified sample): prepared by adding a known mass of target analyte to a specified amount of matrix sample for which an independent estimate of target analyte concentration is available. Matrix spikes are used, for example, to determine the effect of the matrix on a method's recovery efficiency. (Glossary of Quality Assurance Terms, QAMS, 8/31/92).

Matrix Spike Duplicate (spiked sample/fortified sample duplicate): a second replicate matrix spike is prepared in the laboratory and analyzed to obtain a measure of the precision of the recovery for each analyte. (Glossary of Quality Assurance Terms, QAMS, 8/31/92).

May: permitted, but not required (TRADE)

Method Blank: a sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples containing an analyte of interest through all steps of the analytical procedures. (NELAC).

Method Detection Limit: the minimum concentration of a substance (an analyte) that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte. (40 CFR Part 136 Appendix B).

Must: denotes a requirement that must be met. (Random House College Dictionary)

Negative Control: measures taken to ensure that a test, its components, or the environment do not cause undesired effects, or produce incorrect test results.

Performance Audit: the routine comparison of independently obtained quantitative measurement system data with routinely obtained data in order to evaluate the proficiency of an analyst or laboratory.

Positive Control: measures taken to ensure that a test and/or its components are working properly and producing correct or expected results from positive test subjects.

Precision: the degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms..

Preservation: refrigeration and or reagents added at the time of sample collection to maintain the chemical and or biological integrity of the sample.

Proficiency Test Sample (PT): a sample, the composition of which is unknown to the analyst and is provided to test whether the analyst/laboratory can produce analytical results within specified acceptance criteria . (Glossary of Quality Assurance Terms, QAMS, 8/31/92).

Proficiency Testing: Determination of the laboratory calibration or testing performance by means of interlaboratory comparisons. (ISO/IEC Guide 2 - 12.6, amended)

Proficiency Testing Program: the aggregate of providing rigorously controlled and standardized environmental samples to a laboratory for analysis, reporting of results, statistical evaluation of the results in comparison to peer laboratories and the collective demographics and results summary of all participating laboratories.

Protocol: a detailed written procedure for field and/or laboratory operation (e.g., sampling, analysis) which must be strictly followed.

Reagent Water: shall be water in which no target analytes or interferences are present at a concentration which would impact the results when using a particular analytical test method.

Quality Assurance: an integrated system of activities involving planning, quality control, quality assessment, reporting and quality improvement to ensure that a product or service meets defined standards of quality with a stated level of confidence. (Glossary of Quality Assurance Terms, QAMS, 8/31/92).

Quality Control: the overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of users. (Glossary of Quality Assurance Terms, QAMS, 8/31/92).

Quality Manual: A document stating the quality policy, quality system and quality practices of an organization. This may be also called a Quality Assurance Plan or a Quality Plan.
NOTE - The quality manual may call up other documentation relating to the laboratory's quality arrangements.

Quality System: a structured and documented management system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for ensuring quality in its work processes, products (items), and services. The quality system provides the framework for planning, implementing, and assessing work performed by the organization and for carrying out required QA and QC. (ANSI/ASQC E-41994)

Quantitation Limits: the maximum or minimum levels, concentrations, or quantities of a target variable (e.g., target analyte) that can be quantified with the confidence level required by the data user.

Range: the difference between the minimum and the maximum of a set of values.

Raw Data: any original factual information from a measurement activity or study recorded in a laboratory notebook, worksheets, records, memoranda, notes ,or exact copies thereof that are necessary for the reconstruction and evaluation of the report of the activity or study. Raw data may include photography, microfilm or microfiche copies, computer printouts, magnetic media, including dictated observations, and recorded data from automated instruments. If exact copies of raw data have been prepared (e.g., tapes which have been transcribed verbatim, data and verified accurate by signature), the exact copy or exact transcript may be submitted.

Reagent Blank (method reagent blank): a sample consisting of reagent(s), without the target analyte or sample matrix, introduced into the analytical procedure at the appropriate point and carried through all subsequent steps to determine the contribution of the reagents and of the involved analytical steps. (Glossary of Quality Assurance Terms, QAMS, 8/31/92).

Reference Material: a material or substance one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or for assigning values to materials. (ISO Guide 30 - 2.1)

Reference Standard: a standard, generally of the highest metrological quality available at a given location, from which measurements made at that location are derived. (VIM - 6.08)

Requirement: a translation of the needs into a set of individual quantified or descriptive specifications for the characteristics of an entity in order to enable its realization and examination.

Selectivity: (Analytical chemistry) the capability of a test method or instrument to respond to a target substance or constituent in the presence of nontarget substances.

Sensitivity: the capability of a test method or instrument to discriminate between measurement responses representing different levels (e.g., concentrations) of a variable of interest.

Shall: denotes a requirement that is mandatory whenever the criterion for conformance with the specification requires that there be no deviation. This does not prohibit the use of alternative approaches or methods for implementing the specification so long as the requirement is fulfilled. (*Style Manual for Preparation of Proposed American National Standards*, American National Standards Institute, eighth edition, March 1991).

Should: denotes a guideline or recommendation whenever noncompliance with the specification is permissible. (*Style Manual for Preparation of Proposed American National Standards*, American National Standards Institute, eighth edition, March 1991).

Standard Operating Procedures (SOPs): a written document which details the method of an operation, analysis or action whose techniques and procedures are thoroughly prescribed and which is accepted as the method for performing certain routine or repetitive tasks. (Glossary of Quality Assurance Terms, QAMS, 8/31/92).

Spike: a known mass of target analyte added to a blank sample or subsample; used to determine recovery efficiency or for other quality control purposes.

Standard Reference Material (SRM): a certified reference material produced by the U.S. National

Institute of Standards and Technology and characterized for absolute content, independent of analytical test method.

Supervisor (however named): the individual(s) designated as being responsible for a particular area or category of scientific analysis. This responsibility includes direct day-to-day supervision of technical employees, supply and instrument adequacy and upkeep, quality assurance/quality control duties and ascertaining that technical employees have the required balance of education, training and experience to perform the required analyses.

Surrogate: a substance with properties that mimic the analyte of interest. It is unlikely to be found in environment samples and is added to them for quality control purposes. (Glossary of Quality Assurance Terms, QAMS, 8/31/92).

Test: a technical operation that consists of the determination of one or more characteristics or performance of a given product, material, equipment, organism, physical phenomenon, process or service according to a specified procedure.
NOTE - The result of a test is normally recorded in a document sometimes called a test report or a test certificate. (ISO/IEC Guide 2 - 12.1, amended)

Test Method: defined technical procedure for performing a test.

Control Chart: A chart in which the plotted quality control data is assessed via a tolerance level (e.g. +/- 10% of a mean) based on the precision level judged acceptable to meet overall quality/data use requirements instead of a statistical acceptance criteria (e.g. +/- 3 sigma).

Traceability: the property of a result of a measurement whereby it can be related to appropriate standards, generally international or national standards, through an unbroken chain of comparisons. (VIM - 6.12)

Verification: confirmation by examination and provision of evidence that specified requirements have been met.
NOTE - In connection with the management of measuring equipment, verification provides a means for checking that the deviations between values indicated by a measuring instrument and corresponding known values of a measured quantity are consistently smaller than the maximum allowable error defined in a standard, regulation or specification peculiar to the management of the measuring equipment. The result of verification leads to a decision either to restore in service, to perform adjustments, or to repair, or to downgrade, or to declare obsolete. In all cases it is required that a written trace of the verification performed shall be kept on the measuring instrument's individual record.

Validation: the process of substantiating specified performance criteria.

F LABORATORY METHOD STANDARD OPERATING PROCEDURES

United States Environmental Protection Agency

www.epa.gov 1994

Method 200.8, Revision 5.4: Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry

METHOD 200.8

DETERMINATION OF TRACE ELEMENTS IN WATERS AND WASTES BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

Revision 5.4
EMMC Version

S.E. Long (Technology Applications Inc.), T.D. Martin, and E.R. Martin - Method 200.8, Revisions 4.2 and 4.3 (1990)

S.E. Long (Technology Applications Inc.) and T.D. Martin - Method 200.8, Revision 4.4 (1991)

J.T. Creed, C.A. Brockhoff, and T.D. Martin - Method 200.8, Revision 5.4 (1994)

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268
METHOD 200.8

DETERMINATION OF TRACE ELEMENTS IN WATERS AND WASTES BY INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 This method provides procedures for determination of dissolved elements in ground waters, surface waters and drinking water. It may also be used for determination of total recoverable element concentrations in these waters as well as wastewaters, sludges and soils samples. This method is applicable to the following elements:

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
Cadmium	(Cd)	7440-43-9
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Lead	(Pb)	7439-92-1
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Selenium	(Se)	7782-49-2
Silver	(Ag)	7440-22-4
Thallium	(Tl)	7440-28-0
Thorium	(Th)	7440-29-1
Uranium	(U)	7440-61-1
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

Estimated instrument detection limits (IDLs) for these elements are listed in Table 1. These are intended as a guide to instrumental limits typical of a system optimized for multielement determinations and employing commercial instrumentation and pneumatic nebulization sample introduction. However, actual method detection limits (MDLs) and linear working ranges will be dependent on the sample matrix, instrumentation and selected operating conditions. Given in Table 7 are typical MDLs for both total recoverable determinations by "direct analysis" and where sample digestion is employed.

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 Dissolved elements are determined after suitable filtration and acid preservation. In order to reduce potential interferences, dissolved solids should not exceed 0.2% (w/v) (Section 4.1.4).

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 samples have been properly preserved with acid and have turbidity of <1 NTU at the time of analysis. This total recoverable determination procedure is referred to as "direct analysis".

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 (Section 11.2.2).

1.6 The total recoverable sample digestion procedure given in this method is not suitable for the determination of volatile organo-mercury compounds. However, for "direct analysis" of drinking water (turbidity <1 NTU), the combined concentrations of inorganic and organo-mercury in solution can be determined by "direct analysis" pneumatic nebulization provided gold is added to both samples and standards alike to eliminate memory interference effects.

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 sample aliquots must 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.

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 This method should be used by analysts experienced in the use of inductively coupled plasma mass spectrometry (ICP-MS), the interpretation of spectral and matrix interferences and procedures for their correction. A minimum of six months experience with commercial instrumentation is recommended.

1.10 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 method describes the multi-element determination of trace elements by ICP-MS.[1-3] Sample material in solution is introduced by pneumatic nebulization into a radiofrequency plasma where energy transfer processes cause desolvation, atomization and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio by a quadrupole mass spectrometer having a minimum resolution capability of 1 amu peak width at 5% peak height. The ions transmitted through the quadrupole are detected by an electron multiplier or Faraday detector and the ion information processed by a data handling system. Interferences relating to the technique (Section 4.0) must be recognized and corrected for. Such corrections must include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from the plasma gas, reagents or sample matrix. Instrumental drift as well as suppressions or enhancements of instrument response caused by the sample matrix must be corrected for by the use of internal standards.

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 7.6.1).

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 7.4).

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 selected analytical mass(es). (Table 1).

3.6 **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 (Sections 7.5 and 9.4.5).

3.7 **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.

3.8 **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 7.9 and 9.3.2).

3.9 **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).

3.10 **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 7.6.2 and 9.3.1).

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

3.12 **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 7).

3.13 **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 7.8 and 9.2.3).

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

3.15 **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 7.3).

3.16 **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).

3.17 **Tuning Solution** - A solution which is used to determine acceptable instrument performance prior to calibration and sample analyses (Section 7.7).

3.18 **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 Several interference sources may cause inaccuracies in the determination of trace elements by ICP-MS. These are:

4.1.1 Isobaric elemental interferences - Are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio and which cannot be resolved by the mass spectrometer in use. All elements determined by this method have, at a minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this method (Table 4), only molybdenum-98 (ruthenium) and selenium-82 (krypton) have isobaric elemental interferences. If alternative analytical isotopes having higher

natural abundance are selected in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process should be included with the report of the data. It should be noted that such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios should be established prior to the application of any corrections.

4.1.2 Abundance sensitivity - Is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and quadrupole operating pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution adjusted to minimize them.

4.1.3 Isobaric polyatomic ion interferences - Are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer in use. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified[3], and these are listed in Table2 together with the method elements affected. Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence as the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions. In particular, the common ^{82}Kr interference that affects the determination of both arsenic and selenium, can be greatly reduced with the use of high purity krypton free argon.

4.1.4 Physical interferences - Are associated with the physical processes which govern the transport of sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute deposits of material on the extraction and/or skimmer cones reducing the effective diameter of the orifices and therefore ion transmission. Dissolved solids levels not exceeding 0.2% (w/v) have been recommended[3] to reduce such effects. Internal standardization may be effectively used to compensate for many physical interference effects.[4] Internal standards ideally should have similar

analytical behavior to the elements being determined.

4.1.5 Memory interferences - Result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the sampler and skimmer cones, 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 7.6.3). 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 should be estimated prior to analysis. This may be achieved by aspirating a standard containing elements corresponding to 10 times the upper end of the linear range for 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 10 of the method detection limit, should be noted. Memory interferences may also be assessed within an analytical run by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alerted to the possibility of a memory effect, and should examine the analyte concentration in the previous sample to identify if this was high. If a memory interference is suspected, the sample should be reanalyzed after a long rinse period. In the determination of mercury, which suffers from severe memory effects, the addition of 100 µg/L gold will effectively rinse 5 µg/L mercury in approximately two minutes. Higher concentrations will require a longer rinse time.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of reagents 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.[5,8] A reference file of material data handling sheets should also be 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 Analytical plasma sources emit radiofrequency radiation in addition to intense UV radiation. Suitable precautions should be taken to protect personnel from such hazards. The inductively coupled plasma should only be viewed with proper eye protection from UV 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 mass spectrometer:

6.1.1 Instrument capable of scanning the mass range 5-250 amu with a minimum resolution capability of 1 amu peak width at 5% peak height. Instrument may be fitted with a conventional or extended dynamic range detection system.

Note: If an electron multiplier detector is being used, precautions should be taken, where necessary, to prevent exposure to high ion flux. Otherwise changes in instrument response or damage to the multiplier may result.

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 (Section 4.1.3).

6.1.4 A variable-speed peristaltic pump is required for solution delivery to the nebulizer.

6.1.5 A mass-flow controller on the nebulizer gas supply is required. A water-cooled spray chamber may be of benefit in reducing some types of interferences (e.g., from polyatomic oxide species).

6.1.6 If an electron multiplier detector is being used, precautions should be taken, where necessary, to prevent exposure to high ion flux. Otherwise changes in instrument response or damage to the multiplier may result. Samples having high concentrations of elements beyond the linear range of the instrument and with isotopes falling within scanning windows should be diluted prior to analysis.

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 105°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 soaking overnight and thoroughly washing with laboratory-grade detergent and water, rinsing with tap water, and soaking for four hours or more in 20% (V/V) nitric acid or a mixture of dilute nitric and hydrochloric acid (1+2+9), followed by rinsing with reagent grade water and storing clean.

Note: Chromic acid must not be used for cleaning glassware.

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 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 ETFE (ethylene tetrafluorethylene) screw closure, 125-250 mL 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 that might affect the integrity of analytical data. Owing to the high sensitivity of ICP-MS, high-purity reagents should be used whenever possible. All acids used for this method must be of ultra high-purity grade. Suitable acids are available from a number of manufacturers or may be prepared by sub-boiling distillation. Nitric acid is preferred for ICP-MS in order to minimize polyatomic ion interferences. Several polyatomic ion interferences result when hydrochloric acid is used (Table 2), however, it should be noted that hydrochloric acid is required to maintain stability in solutions containing antimony and silver. When hydrochloric acid is used, corrections for the chloride polyatomic ion interferences must be applied to all data.

7.1.1 Nitric acid, concentrated (sp.gr. 1.41).

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

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

7.1.4 Hydrochloric acid, concentrated (sp.gr. 1.19).

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

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

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

7.1.8 Tartaric acid (CASRN 87-69-4).

7.2 Reagent water - All references to reagent grade water in this method refer to ASTM Type I water (ASTM D1193).[9] Suitable water may be prepared by passing distilled water through a mixed bed of anion and cation exchange resins.

7.3 Standard Stock Solutions - Stock standards may be purchased from a reputable commercial source or prepared from ultra high-purity grade chemicals or metals (99.99-99.999% pure). All salts should be dried for one hour at 105°C, unless otherwise specified. Stock solutions should be stored in FEP bottles. Replace stock standards when succeeding dilutions for preparation of the multielement stock standards can not be verified.

CAUTION: Many metal salts are extremely toxic if inhaled or swallowed. Wash hands thoroughly after handling.

The following procedures may be used for preparing standard stock solutions:

Note: Some metals, particularly those which form surface oxides require cleaning prior to being weighed. This may be achieved by pickling the surface of the metal in acid. An amount in excess of the desired weight should be pickled repeatedly, rinsed with water, dried and weighed until the desired weight is achieved.

7.3.1 Aluminum solution, stock 1 mL = 1000 µg Al: Pickle aluminum metal in warm (1+1) HCl to an exact weight of 0.100 g. Dissolve in 10 mL conc. HCl and 2 mL conc. nitric acid, heating to effect solution. Continue heating until volume is reduced to 4 mL. Cool and add 4 mL reagent grade water. Heat until the volume is reduced to 2 mL. Cool and dilute to 100 mL with reagent grade water.

7.3.2 Antimony solution, stock 1 mL = 1000 µg Sb: Dissolve 0.100 g antimony powder in 2 mL (1+1) nitric acid and 0.5 mL conc. hydrochloric acid, heating to effect solution. Cool, add 20 mL reagent grade water and 0.15 g tartaric acid. Warm the solution to dissolve the white precipitate. Cool and dilute to 100 mL with reagent grade water.

7.3.3 Arsenic solution, stock 1 mL = 1000 µg As: Dissolve 0.1320 g As_2O_3 in a mixture of 50 mL reagent grade water and 1 mL conc. ammonium hydroxide. Heat gently to dissolve. Cool and acidify the solution with 2 mL conc. nitric acid. Dilute to 100 mL with reagent grade water.

7.3.4 Barium solution, stock 1 mL = 1000 µg Ba: Dissolve 0.1437 g $BaCO_3$ in a solution mixture of 10 mL reagent grade water and 2 mL conc. nitric acid. Heat and stir to effect solution and degassing. Dilute to 100 mL with reagent grade water.

7.3.5 Beryllium solution, stock 1 mL = 1000 µg Be: Dissolve 1.965 g $BeSO_4 \bullet 4H_2O$ (DO NOT DRY) in 50 mL reagent grade water. Add 1 mL conc. nitric acid. Dilute to 100 mL with reagent grade water.

7.3.6 Bismuth solution, stock 1 mL = 1000 µg Bi: Dissolve 0.1115 g Bi_2O_3 in 5 mL conc. nitric acid. Heat to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.7 Cadmium solution, stock 1 mL = 1000 µg Cd: Pickle cadmium metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.8 Chromium solution, stock 1 mL = 1000 µg Cr: Dissolve 0.1923 g CrO_3 in a solution mixture of 10 mL reagent grade water and 1 mL conc. nitric

acid. Dilute to 100 mL with reagent grade water.

7.3.9 Cobalt solution, stock 1 mL = 1000 µg Co: Pickle cobalt metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.10 Copper solution, stock 1 mL = 1000 µg Cu: Pickle copper metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.11 Gold solution, stock 1 mL = 1000 µg Au: Dissolve 0.100 g high purity (99.9999%) Au shot in 10 mL of hot conc. nitric acid by dropwise addition of 5 mL conc. HCl and then reflux to expel oxides of nitrogen and chlorine. Cool and dilute to 100 mL with reagent grade water.

7.3.12 Indium solution, stock 1 mL = 1000 µg In: Pickle indium metal in (1+1) nitric acid to an exact weight of 0.100 g. Dissolve in 10 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.13 Lead solution, stock 1 mL = 1000 µg Pb: Dissolve 0.1599 g $PbNO_3$ in 5 mL (1+1) nitric acid. Dilute to 100 mL with reagent grade water.

7.3.14 Magnesium solution, stock 1 mL = 1000 µg Mg: Dissolve 0.1658 g MgO in 10 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.15 Manganese solution, stock 1 mL = 1000 µg Mn: Pickle manganese flake in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.16 Mercury solution, stock, 1 mL = 1000 µg Hg: DO NOT DRY. **CAUTION**: highly toxic element. Dissolve 0.1354 g $HgCl_2$ in reagent water. Add 5.0 mL concentrated HNO_3 and dilute to 100 mL with reagent water.

7.3.17 Molybdenum solution, stock 1 mL = 1000 µg Mo: Dissolve 0.1500 g MoO_3 in a solution mixture of 10 mL reagent grade water and 1 mL conc. ammonium hydroxide., heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.18 Nickel solution, stock 1 mL = 1000 µg Ni: Dissolve 0.100 g nickel powder in 5 mL conc. nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.19 Scandium solution, stock 1 mL = 1000 µg Sc: Dissolve 0.1534 g Sc_2O_3 in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to

100 mL with reagent grade water.

7.3.20 Selenium solution, stock 1 mL = 1000 µg Se: Dissolve 0.1405 g SeO_2 in 20 mL ASTM Type I water. Dilute to 100 mL with reagent grade water.

7.3.21 Silver solution, stock 1 mL = 1000 µg Ag: Dissolve 0.100 g silver metal in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water. Store in dark container.

7.3.22 Terbium solution, stock 1 mL = 1000 µg Tb: Dissolve 0.1176 g Tb_4O_7 in 5 mL conc. nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.23 Thallium solution, stock 1 mL = 1000 µg Tl: Dissolve 0.1303 g $TlNO_3$ in a solution mixture of 10 mL reagent grade water and 1 mL conc. nitric acid. Dilute to 100 mL with reagent grade water.

7.3.24 Thorium solution, stock 1 mL = 1000 µg Th: Dissolve 0.2380 g $Th(NO_3)_4 \cdot 4H_2O$ (DO NOT DRY) in 20 mL reagent grade water. Dilute to 100 mL with reagent grade water.

7.3.25 Uranium solution, stock 1 mL = 1000 µg U: Dissolve 0.2110 g $UO_2(NO_3)_2 \cdot 6H_2O$ (DO NOT DRY) in 20 mL reagent grade water and dilute to 100 mL with reagent grade water.

7.3.26 Vanadium solution, stock 1 mL = 1000 µg V: Pickle vanadium metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.27 Yttrium solution, stock 1 mL = 1000 µg Y: Dissolve 0.1270 g Y_2O_3 in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.3.28 Zinc solution, stock 1 mL = 1000 µg Zn: Pickle zinc metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent grade water.

7.4 Multielement Stock Standard Solutions - Care must be taken in the preparation of multielement stock standards that the elements are compatible and stable. Originating element stocks should be checked for the presence of impurities which might influence the accuracy of the standard. Freshly prepared standards should be transferred to acid cleaned, not previously used FEP fluorocarbon bottles for storage and monitored periodically for stability. The following combinations of elements are suggested:

Standard Solution A		Standard Solution B
Aluminum	Mercury	Barium
Antimony	Molybdenum	Silver
Arsenic	Nickel	
Beryllium	Selenium	
Cadmium	Thallium	
Chromium	Thorium	
Cobalt	Uranium	
Copper	Vanadium	
Lead	Zinc	
Manganese		

Except for selenium and mercury, multielement stock standard solutions A and B (1 mL = 10 µg) may be prepared by diluting 1.0 mL of each single element stock standard in the combination list to 100 mL with reagent water containing 1% (v/v) nitric acid. For mercury and selenium in solution A, aliquots of 0.05 mL and 5.0 mL of the respective stock standards should be diluted to the specified 100 mL (1 ml = 0.5 µg Hg and 50 µg Se). Replace the multielement stock standards when succeeding dilutions for preparation of the calibration standards cannot be verified with the quality control sample.

7.4.1 Preparation of calibration standards - fresh multielement calibration standards should be prepared every two weeks or as needed. Dilute each of the stock multielement standard solutions A and B to levels appropriate to the operating range of the instrument using reagent water containing 1% (v/v) nitric acid. The element concentrations in the standards should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve. Depending on the sensitivity of the instrument, concentrations ranging from 10-200 µg/L are suggested, except mercury, which should be limited to ≤5 µg/L. It should be noted the selenium concentration is always a factor of 5 greater than the other analytes. If the direct addition procedure is being used (Method A, Section 10.3), add internal standards (Section 7.5) to the calibration standards and store in FEP bottles. Calibration standards should be verified initially using a quality control sample (Section 7.8).

7.5 Internal Standards Stock Solution - 1 mL = 100 µg. Dilute 10 mL of scandium, yttrium, indium, terbium and bismuth stock standards (Section 7.3) to 100 mL with reagent water, and store in a FEP bottle. Use this solution concentrate for addition to blanks, calibration standards and samples, or dilute by an appropriate amount using 1% (v/v) nitric acid, if the internal standards are being added by peristaltic pump (Method B, Section 10.3).

Note: If mercury is to be determined by the "direct analysis" procedure, add an aliquot of the gold stock standard (Section 7.3.11) to the internal standard solution sufficient to provide a concentration of 100 µg/L in final the dilution of all blanks, calibration standards, and samples.

7.6 Blanks - Three types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, the laboratory reagent blank is used to assess possible contamination from the sample preparation procedure and to assess spectral background and the rinse blank is used to flush the instrument between samples in order to reduce memory interferences.

7.6.1 Calibration blank - Consists of 1% (v/v) nitric acid in reagent grade water. If the direct addition procedure (Method A, Section 10.3) is being used, add internal standards.

7.6.2 Laboratory reagent blank (LRB) - Must contain all the reagents in the same volumes as used in processing the samples. The LRB must be carried through the same entire preparation scheme as the samples including digestion, when applicable. If the direct addition procedure (Method A, Section 10.3) is being used, add internal standards to the solution after preparation is complete.

7.6.3 Rinse blank - Consists of 2% (v/v) nitric acid in reagent grade water.

Note: If mercury is to be determined by the "direct analysis" procedure, add gold (Section 7.3.11) to the rinse blank to a concentration of 100 µg/L.

7.7 Tuning Solution - This solution is used for instrument tuning and mass calibration prior to analysis. The solution is prepared by mixing beryllium, magnesium, cobalt, indium and lead stock solutions (Section 7.3) in 1% (v/v) nitric acid to produce a concentration of 100 µg/L of each element. Internal standards are not added to this solution. (Depending on the sensitivity of the instrument, this solution may need to be diluted 10-fold.)

7.8 Quality Control Sample (QCS) - The QCS should be obtained from a source outside the laboratory. The concentration of the QCS solution analyzed will depend on the sensitivity of the instrument. To prepare the QCS dilute an appropriate aliquot of analytes to a concentration ≤100 µg/L in 1% (v/v) nitric acid. Because of lower sensitivity, selenium may be diluted to a concentration of <500 µg/L, however, in all cases, mercury should be limited to a concentration of ≤5 µg/L. If the direct addition procedure (Method A, Section 10.3) is being used, add internal standards after dilution, mix and store in a FEP bottle. The QCS should be analyzed as needed to meet data-quality needs and a fresh solution should be prepared quarterly or more frequently as needed.

7.9 Laboratory Fortified Blank (LFB) - To an aliquot of LRB, add aliquots from multielement stock standards A and B (Section 7.4) to prepared the LFB. Depending on the sensitivity of the instrument, the fortified concentration used should range from 40-100 µg/L for each analyte, except selenium and mercury. For selenium the concentration should range from 200-500 µg/L, while the concentration range mercury should be limited to 2-5 µg/L. The LFB must be carried through the same entire preparation scheme as the samples including sample digestion, when applicable. If the direct addition procedure (Method A, Section 10.3) is being used, add internal standards to this solution after

preparation has been completed.

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 6 months before analysis.

8.2 For the determination of 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. Use a portion of the 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 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 calibration 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 calibration 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 calibration ranges - Linear calibration ranges are primarily detector limited. The upper limit of the linear calibration range should be established for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range. Care should be taken to avoid potential damage to the detector during this process. The linear calibration range which may be used for the analysis of samples should be judged by the analyst from the resulting data. The upper LDR limit should be an observed signal no more than 10% below the level extrapolated from lower standards. 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 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 or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS (Section 7.8). To verify the calibration standards the determined mean concentration from three analyses of the QCS must be within ±10% of the stated QCS value. If the QCS is used for determining acceptable on-going instrument performance, analysis of the QCS prepared to a concentration of 100 µg/L must be within ±10% of the stated value or within the acceptance limits listed in Table 8, whichever is the greater. (If the QCS is not within the required limits, an immediate second analysis of the QCS is recommended to confirm unacceptable performance.) If the calibration standards and/or acceptable instrument performance cannot be verified, 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 limits (MDL) should be established for all analytes, using reagent water (blank) fortified at a concentration of two to five times the estimated detection limit.[7] 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 = Student's 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) can give confidence to the MDL value determined in reagent water. Typical single laboratory MDL values using this method are given in Table 7.

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 7.6.2) with each batch of 20 or fewer of samples of the same matrix. LRB data are used to assess contamination from the laboratory environment and to characterize spectral background from the reagents used in sample processing. 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 7.9) 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:

$$\text{UPPER CONTROL LIMIT} = x + 3S$$
$$\text{LOWER CONTROL LIMIT} = x - 3S$$

The optional control limits must be equal to or better than the required control limits of 85-115%. After each five to ten 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 - For all determinations the laboratory must check instrument performance and verify that the instrument is properly calibrated on a continuing basis. To verify calibration run the calibration blank and calibration standards as surrogate samples immediately following each calibration routine, after every ten analyses and at the end of the sample run. The results of the analyses of the standards will indicate whether the calibration remains valid. The analysis of all analytes within the standard solutions must be within ±10% of calibration. If the calibration cannot be verified within the specified limits, the instrument must be recalibrated. (The instrument responses from the calibration check may be used for recalibration purposes, however, it must be verified before continuing sample analysis.) If the continuing calibration check is not confirmed within ±15%, the previous 10 samples must be reanalyzed after recalibration. If the sample matrix is responsible for the calibration drift, it is recommended that the previous 10 samples are reanalyzed in groups of five between calibration checks to prevent a similar drift situation from occurring.

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.

9.4.2 The laboratory must add a known amount of 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 7.9). For solid samples, the concentration added should be 100 mg/kg equivalent (200 µg/L in the analysis solution) except silver which should be limited to 50 mg/kg (Section 1.8). Over time, samples from all routine sample sources should be fortified.

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%. Recovery calculations are not required if the concentration of the analyte 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:

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

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 recovery of any analyte falls outside the designated range and 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 an uncorrected matrix effect.

9.4.5 Internal standards responses - The analyst is expected to monitor the responses from the internal standards throughout the sample set being

analyzed. Ratios of the internal standards responses against each other should also be monitored routinely. This information may be used to detect potential problems caused by mass dependent drift, errors incurred in adding the internal standards or increases in the concentrations of individual internal standards caused by background contributions from the sample. The absolute response of any one internal standard must not deviate more than 60-125% of the original response in the calibration blank. If deviations greater than these are observed, flush the instrument with the rinse blank and monitor the responses in the calibration blank. If the responses of the internal standards are now within the limit, take a fresh aliquot of the sample, dilute by a further factor of two, add the internal standards and reanalyze. If after flushing the response of the internal standards in the calibration blank are out of limits, terminate the analysis and determine the cause of the drift. Possible causes of drift may be a partially blocked sampling cone or a change in the tuning condition of the instrument.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Operating conditions - Because of the diversity of instrument hardware, no detailed instrument operating conditions are provided. The analyst is advised to follow the recommended operating conditions provided by the manufacturer. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions satisfy the analytical requirements and to maintain quality control data verifying instrument performance and analytical results. Instrument operating conditions which were used to generate precision and recovery data for this method (Section 13.0) are included in Table 6.

10.2 Precalibration routine - The following precalibration routine must be completed prior to calibrating the instrument until such time it can be documented with periodic performance data that the instrument meets the criteria listed below without daily tuning.

10.2.1 Initiate proper operating configuration of instrument and data system. Allow a period of not less than 30 minutes for the instrument to warm up. During this process conduct mass calibration and resolution checks using the tuning solution. Resolution at low mass is indicated by magnesium isotopes 24, 25, and 26. Resolution at high mass is indicated by lead isotopes 206, 207, and 208. For good performance adjust spectrometer resolution to produce a peak width of approximately 0.75 amu at 5% peak height. Adjust mass calibration if it has shifted by more than 0.1 amu from unit mass.

10.2.2 Instrument stability must be demonstrated by running the tuning solution (Section 7.7) a minimum of five times with resulting relative standard deviations of absolute signals for all analytes of less than 5%.

10.3 Internal Standardization - Internal standardization must be used in all analyses to correct for instrument drift and physical interferences. A list of acceptable

internal standards is provided in Table 3. For full mass range scans, a minimum of three internal standards must be used. Procedures described in this method for general application, detail the use of five internal standards; scandium, yttrium, indium, terbium and bismuth. These were used to generate the precision and recovery data attached to this method. Internal standards must be present in all samples, standards and blanks at identical levels. This may be achieved by directly adding an aliquot of the internal standards to the CAL standard, blank or sample solution (Method A, Section 10.3), or alternatively by mixing with the solution prior to nebulization using a second channel of the peristaltic pump and a mixing coil (Method B, Section 10.3). The concentration of the internal standard should be sufficiently high that good precision is obtained in the measurement of the isotope used for data correction and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. Depending on the sensitivity of the instrument, a concentration range of 20-200 µg/L of each internal standard is recommended. Internal standards should be added to blanks, samples and standards in a like manner, so that dilution effects resulting from the addition may be disregarded.

10.4 Calibration - Prior to initial calibration, set up proper instrument software routines for quantitative analysis. The instrument must be calibrated using one of the internal standard routines (Method A or B) described in Section 10.3. The instrument must be calibrated for the analytes to be determined using the calibration blank (Section 7.6.1) and calibration standards A and B (Section 7.4.1) prepared at one or more concentration levels. A minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for instrument calibration and data reporting.

10.5 The rinse blank should be used to flush the system between solution changes for blanks, standards and samples. Allow sufficient rinse time to remove traces of the previous sample (Section 4.1.5). Solutions should be aspirated for 30 seconds prior to the acquisition of data to allow equilibrium to be established.

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). If the direct addition procedure (Method A, Section 10.3) is being used, add internal standards, cap the tube and mix. The sample is now ready for analysis (Section 1.2). Allowance for sample dilution should be made in the calculations.

Note: If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be treated using the procedure in Section 11.2 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. 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 11.2.8.

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, 1.7, and 1.8). (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 11.3.7.

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 or 50 mL class A stoppered graduated cylinder, 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.)

11.2.8 Prior to analysis, adjust the chloride concentration by pipetting 20 mL of the prepared solution into a 50 mL volumetric flask, dilute to volume with reagent water and mix. (If the dissolved solids in this solution are >0.2%, additional dilution may be required to prevent clogging of the extraction and/or skimmer cones. If the direct addition procedure (Method A, Section 10.3) is being used, add internal standards and mix. 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.

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.)

11.3.7 Prior to analysis, adjust the chloride concentration by pipetting 20 mL of the prepared solution into a 100 mL volumetric flask, dilute to volume with reagent water and mix. (If the dissolved solids in this solution are >0.2%, additional dilution may be required to prevent clogging of the extraction and/or skimmer cones. If the direct addition procedure (Method A, Section 10.3) is being used, add internal standards and mix. 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.

Note: Determine the percent solids in the sample for use in calculations and for reporting data on a dry weight basis.

11.4 Sample Analysis

11.4.1 For every new or unusual matrix, it is highly recommended that a semi-quantitative analysis be carried out to screen the sample for elements at high concentration. Information gained from this may be used to prevent potential damage to the detector during sample analysis and to identify elements which may be higher than the linear range. Matrix screening may be carried out by using intelligent software, if available, or by diluting the sample by a factor of 500 and analyzing in a semi-quantitative mode. The sample should also be screened for background levels of all elements chosen for use as internal standards in order to prevent bias in the calculation of the analytical data.

11.4.2 Initiate instrument operating configuration. Tune and calibrate the instrument for the analytes of interest (Section 10.0).

11.4.3 Establish instrument software run procedures for quantitative analysis. For all sample analyses, a minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for data reporting.

11.4.4 All masses which might affect data quality must be monitored during the analytical run. As a minimum, those masses prescribed in Table 4 must be monitored in the same scan as is used for the collection of the data. This information should be used to correct the data for identified interferences.

11.4.5 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.

11.4.6 The rinse blank should be used to flush the system between samples. Allow sufficient time to remove traces of the previous sample or a minimum of one minute (Section 4.1.5). Samples should be aspirated for 30 seconds prior to the collection of data.

11.4.7 Samples having concentrations higher than the established linear dynamic range should be diluted into range and reanalyzed. The sample should first be analyzed for the trace elements in the sample, protecting the detector from the high concentration elements, if necessary, by the selection of appropriate scanning windows. The sample should then be diluted for the determination of the remaining elements. Alternatively, the dynamic range may be adjusted by selecting an alternative isotope of lower natural abundance, provided quality control data for that isotope have been established. The dynamic range must not be adjusted by altering instrument conditions to an uncharacterized state.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Elemental equations recommended for sample data calculations are listed in Table 5. Sample data should be reported in units of µg/L for aqueous samples or mg/kg dry weight for solid samples. Do not report element concentrations below the determined MDL.

12.2 For data values less than 10, two significant figures should be used for reporting element concentrations. For data values greater than or equal to 10, three significant figures should be used.

12.3 For aqueous samples prepared by total recoverable procedure (Section 11.2), multiply solution concentrations by the dilution factor 1.25. If additional dilutions were made to any samples or an aqueous sample was prepared using the acid-mixture procedure described in Section 11.3, the appropriate factor should be applied to the calculated sample concentrations.

12.4 For total recoverable analytes in solid samples (Section 11.3), round the solution analyte concentrations (µg/L in the analysis solution) as instructed in Section 12.2. Multiply the µ/L concentrations in the analysis solution by the factor 0.005 to calculate the mg/L analyte concentration in the 100 mL extract solution. (If additional dilutions were made to any samples, the appropriate factor should be applied to calculate analyte concentrations in the extract solution.) 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:

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

where:

C = Concentration in the extract (mg/L)
V = Volume of extract (L, 100 mL = 0.1L)
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.

12.5 To report percent solids in solid samples (Sect. 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.

12.6 Data values should be corrected for instrument drift or sample matrix induced interferences by the application of internal standardization. Corrections for characterized spectral interferences should be applied to the data. Chloride interference corrections should be made on all samples, regardless of the addition of hydrochloric acid, as the chloride ion is a common constituent of environmental samples.

12.7 If an element has more than one monitored isotope, examination of the concentration calculated for each isotope, or the isotope ratios, will provide useful information for the analyst in detecting a possible spectral interference.

Consideration should therefore be given to both primary and secondary isotopes in the evaluation of the element concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes, therefore differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.

12.8 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 Instrument operating conditions used for single laboratory testing of the method are summarized in Table 6. Total recoverable digestion and "direct analysis" MDLs determined using the procedure described in Section 9.2.4, are listed in Table 7.

13.2 Data obtained from single laboratory testing of the method are summarized in Table 9 for five water samples representing drinking water, surface water, ground water and waste effluent. Samples were prepared using the procedure described in Section 11.2. For each matrix, five replicates were analyzed and the average of the replicates used for determining the sample background concentration for each element. Two further pairs of duplicates were fortified at different concentration levels. For each method element, the sample background concentration, mean percent recovery, the standard deviation of the percent recovery and the relative percent difference between the duplicate fortified samples are listed in Table 8.

13.3 Data obtained from single laboratory testing of the method are summarized in Table 10 for three solid samples consisting of SRM 1645 River Sediment, EPA Hazardous Soil and EPA Electroplating Sludge. Samples were prepared using the procedure described in Section 11.3. For each method element, the sample background concentration, mean percent recovery, the standard deviation of the percent recovery and the relative percent difference between the duplicate fortified samples were determined as for Section 13.2.

13.4 Data obtained from single laboratory testing of the method for drinking water analysis using the "direct analysis" procedure (Section 11.2.1) are given in Table 11. Three drinking water samples of varying hardness collected from Regions 4, 6, and 10 were fortified to contain 1 µg/L of all metal primary contaminants, except selenium, which was added to a concentration of 20 µg/L. For each matrix, four replicate aliquots were analyzed to determine the sample background concentration of each analyte and four fortified aliquots were analyzed to determine mean percent recovery in each matrix. Listed in the Table 11 are the average mean percent recovery of each analyte in the three matrices and the standard deviation of the mean percent recoveries.

13.5 Listed in Table 12 are the regression equations for precision and bias developed from the joint USEPA/Association of Official Analytical Chemists (AOAC) multilaboratory validation study conducted on this method. These equations

were developed from data received from 13 laboratories on reagent water, drinking water and ground water. Listed in Tables 13 and 14, respectively, are the precision and recovery data from a wastewater digestate supplied to all laboratories and from a wastewater of the participant's choice. For a complete review of the study see Reference 11, Section 16.0 of this method.

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. 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: ESTIMATED INSTRUMENT DETECTION LIMITS

Element	Recommended Analytical Mass	Scanning Mode[1]	Selection Ion Monitoring Mode[2,3]
Aluminum	27	0.05	0.02
Antimony	123	0.08	0.008
Arsenic(3)	75	0.9	0.02
Barium	137	0.5	0.03
Beryllium	9	0.1	0.02
Cadmium	111	0.1	0.02
Chromium	52	0.07	0.04
Cobalt	59	0.03	0.002
Copper	63	0.03	0.004
Lead	206, 207, 208	0.08	0.015
Manganese	55	0.1	0.007
Mercury	202	n.a	0.2
Molybdenum	98	0.1	0.005
Nickel	60	0.2	0.07
Selenium(3)	82	5	1.3
Silver	107	0.05	0.004
Thallium	205	0.09	0.014
Thorium	232	0.03	0.005
Uranium	238	0.02	0.005
Vanadium	51	0.02	0.006
Zinc	66	0.2	0.07

Instrument detection limits (3σ) estimated from seven replicate integrations of the blank (1% v/v nitric acid) following calibration of the instrument with three replicate integrations of a multi-element standard.

[1]Instrument operating conditions and data acquisition mode are given in Table 6.

[2]IDLs determined using state-of-the-art instrumentation (1994). Data for ^{75}As, ^{77}Se, and ^{82}Se were acquired using a dwell time of 4.096 seconds with 1500 area count per sec ^{83}Kr present in argon supply. All other data were acquired using a dwell time of 1.024 seconds per AMU monitored.

TABLE 2: COMMON MOLECULAR ION INTERFERENCES IN ICP-MS

BACKGROUND MOLECULAR IONS		
Molecular Ion	**Mass**	**Element Interference[a]**
NH^+	15	
OH^+	17	
OH_2^+	18	
C_2^+	24	
CN^+	26	
CO^+	28	
N_2^+	28	
N_2H^+	29	
NO^+	30	
NOH^+	31	
O_2^+	32	
O_2H^+	33	
$^{36}ArH^+$	37	
$^{38}ArH^+$	39	
$^{40}ArH^+$	41	
CO_2^+	44	
CO_2H^+	45	Sc
ArC^+, ArO^+	52	Cr
ArN^+	54	Cr
$ArNH^+$	55	Mn
ArO^+	56	
$ArOH^+$	57	
$^{40}Ar^{36}Ar^+$	76	Se
$^{40}Ar^{38}Ar^+$	78	Se
$^{40}Ar^+$	80	Se

[a]method elements or internal standards affected by the molecular ions.

TABLE 2: COMMON MOLECULAR ION INTERFERENCES IN ICP-MS (Cont'd)

MATRIX MOLECULAR IONS

Molecular Ion		Mass	Element Interference[a]
Bromide[12]			
	$^{81}BrH^+$	82	Se
	$^{79}BrO^+$	95	Mo
	$^{81}BrO^+$	97	Mo
	$^{81}BrOH^+$	98	Mo
	$Ar^{81}Br^+$	121	Sb
Chloride			
	$^{35}ClO^+$	51	V
	$^{35}ClOH^+$	52	Cr
	$^{37}ClO^+$	53	Cr
	$^{37}ClOH^+$	54	Cr
	$Ar^{35}Cl^+$	75	As
	$Ar^{37}Cl^+$	77	Se
Sulphate			
	$^{32}SO^+$	48	
	$^{32}SOH^+$	49	
	$^{34}SO^+$	50	V, Cr
	$^{34}SOH^+$	51	V
	SO_2^+, S_2^+	64	Zn
	$Ar^{32}S^+$	72	
	$Ar^{34}S^+$	74	
Phosphate			
	PO^+	47	
	POH^+	48	
	PO_2^+	63	Cu
	ArP^+	71	
Group I, II Metals			
	$ArNa^+$	63	Cu
	ArK^+	79	
	$ArCa^+$	80	

TABLE 2: COMMON MOLECULAR ION INTERFERENCES IN ICP-MS (Cont'd)

MATRIX MOLECULAR IONS		
Molecular Ion	**Mass**	**Element Interference[a]**
Matrix Oxides[*]		
TiO	62-66	Ni, Cu, Zn
ZrO	106-112	Ag, Cd
MoO	108-116	Cd

[*]Oxide interferences will normally be very small and will only impact the method elements when present at relatively high concentrations. Some examples of matrix oxides are listed of which the analyst should be aware. It is recommended that Ti and Zr isotopes are monitored in solid waste samples, which are likely to contain high levels of these elements. Mo is monitored as a method analyte.

TABLE 3: INTERNAL STANDARDS AND LIMITATIONS OF USE

Internal Standard	Mass	Possible Limitation
^{6}Lithium	6	a
Scandium	45	polyatomic ion interference
Yttrium	89	a,b
Rhodium	103	
Indium	115	isobaric interference by Sn
Terbium	159	
Holmium	165	
Lutetium	175	
Bismuth	209	a

a May be present in environmental samples.

b In some instruments Yttrium may form measurable amounts of YO^{+} (105 amu)and YOH^{+} (106 amu). If this is the case, care should be taken in the use of the cadmium elemental correction equation.

Internal standards recommended for use with this method are shown in bold face. Preparation procedures for these are included in Section 7.3.

TABLE 4: RECOMMENDED ANALYTICAL ISOTOPES AND ADDITIONAL MASSES WHICH MUST BE MONITORED

Isotope	Element of Interest
27	Aluminum
121, 123	Antimony
75	Arsenic
135, 137	Barium
9	Beryllium
106, 108, 111, 114	Cadmium
52, 53	Chromium
59	Cobalt
63, 65	Copper
206, 207, 208	Lead
55	Manganese
95, 97, 98	Molybdenum
60, 62	Nickel
77, 82	Selenium
107, 109	Silver
203, 205	Thallium
232	Thorium
238	Uranium
51	Vanadium
66, 67, 68	Zinc
83	Krypton
99	Ruthenium
105	Palladium
118	Tin

NOTE: Isotopes recommended for analytical determination are underlined.

TABLE 5: RECOMMENDED ELEMENTAL EQUATIONS FOR DATA CALCULATIONS

Element	Elemental Equation	Note
Al	(1.000) (^{27}C)	
Sb	(1.000) (^{123}C)	
As	(1.000) (^{75}C)-(3.127) [(^{77}C)-(0.815) (^{82}C)]	(1)
Ba	(1.000) (^{137}C)	
Be	(1.000) (^{9}C)	
Cd	(1.000) (^{111}C)-(1.073) [(^{108}C)-(0.712) (^{106}C)]	(2)
Cr	(1.000) (^{52}C)	(3)
Co	(1.000) (^{59}C)	
Cu	(1.000) (^{63}C)	
Pb	(1.000) (^{206}C)+(1.000) [(^{207}C)+(1.000) (^{208}C)]	(4)
Mn	(1.000) (^{55}C)	
Mo	(1.000) (^{98}C)-(0.146) (^{99}C)	(5)
Ni	(1.000) (^{60}C)	
Se	(1.000) (^{82}C)	(6)
Ag	(1.000) (^{107}C)	
Tl	(1.000) (^{205}C)	
Th	(1.000) (^{232}C)	
U	(1.000) (^{238}C)	
V	(1.000) (^{51}C)-(3.127) [(^{53}C)-(0.113) (^{52}C)]	(7)
Zn	(1.000) (^{66}C)	

TABLE 5: RECOMMENDED ELEMENTAL EQUATIONS FOR DATA CALCULATIONS

Element	Elemental Equation	Note
Bi	(1.000) (^{209}C)	
In	(1.000) (^{209}C)-(0.016) (^{118}C)	(8)
Sc	(1.000) (^{45}C)	
Tb	(1.000) (^{159}C)	
Y	(1.000) (^{89}C)	

C - Calibration blank subtracted counts at specified mass.

(1) - Correction for chloride interference with adjustment for ^{77}Se. ArCl 75/77 ratio may be determined from the reagent blank. Isobaric mass 82 must be from Se only and not BrH^+.

(2) - Correction for MoO interference. Isobaric mass 106 must be from Cd only not ZrO^+. An additional isobaric elemental correction should be made if palladium is present.

(3) - In 0.4% v/v HCl, the background from ClOH will normally be small. However the contribution may be estimated from the reagent blank. Isobaric mass must be from Cr only not ArC^+.

(4) - Allowance for isotopic variability of lead isotopes.

(5) - Isobaric elemental correction for ruthenium.

(6) - Some argon supplies contain krypton as an impurity. Selenium is corrected for ^{82}Kr by background subtraction.

(7) - Correction for chloride interference with adjustment for ^{53}Cr. ClO 51/53 ratio may be determined from the reagent blank. Isobaric mass 52 must be from Cr only not ArC^+.

(8) - Isobaric elemental correction for tin.

TABLE 6: INSTRUMENT OPERATING CONDITIONS FOR PRECISION AND RECOVERY DATA[1]

Instrument	VG PlasmaQuad Type I
Plasma foward power	1.35 kW
Coolant flow rate	13.5 L/min.
Auxillary flow rate	0.6 L/min.
Nebulizer flow rate	0.78 L/min.
Solution uptake rate	0.6 mL/min.
Spray chamber temperature	15°C
Data Acquistion	
Detector mode	Pulse counting
Replicate integrations	3
Mass range	8-240 amu
Dwell time	320 µs
Number of MCA channels	2048
Number of scan sweeps	85
Total acquisition time	3 minutes per sample

[1]The described instrument and operating conditions were used to determine the scanning mode MDL data listed in Table 7 and the precision and recovery data given in Tables 9 and 10.

TABLE 7: METHOD DETECTION LIMITS

	Scanning Mode[1] Total Recoverable		Selection Ion Monitoring Mode[2] Total Recoverable	Direct Analysis[3]
AMU Element	Aqueous µg/L	Solids mg/kg	Aqueous µg/L	Aqueous µg/L
27 Al	1.0	0.4	1.7	0.04
123 Sb	0.4	0.2	0.04	0.02
75 As	1.4	0.6	0.4	0.1
137 Ba	0.8	0.4	0.04	0.04
9 Be	0.3	0.1	0.02	0.03
111 Cd	0.5	0.2	0.03	0.03
52 Cr	0.9	0.4	0.08	0.08
59 Co	0.09	0.04	0.004	0.003
63 Cu	0.5	0.2	0.02	0.01
206,207,208 Pb	0.6	0.3	0.05	0.02
55 Mn	0.1	0.05	0.02	0.04
202 Hg	n.a.	n.a.	n.a	0.2
98 Mo	0.3	0.1	0.01	0.01
60 Ni	0.5	0.2	0.06	0.03
82 Se	7.9	3.2	2.1	0.5
107 Ag	0.1	0.05	0.005	0.005
205 Tl	0.3	0.1	0.02	0.01
232 Th	0.1	0.05	0.02	0.01
238 U	0.1	0.05	0.01	0.01
51 V	2.5	1.0	0.9	0.05
66 Zn	1.8	0.7	0.1	0.2

[1]Data acquisition mode given in Table 6. Total recoverable MDL concentrations are computed for original matrix with allowance for sample dilution during preparation. Listed MDLs for solids calculated from determined aqueous MDLs.

[2]MDLs determined using state-of-the-art instrumentation (1994). Data for ^{75}As, ^{77}Se, and ^{82}Se were acquired using a dwell time of 4.096 seconds with 1500 area count per seconds ^{83}Kr present in argon supply. All other data were acquired using a dwell time of 1.024 seconds per AMU monitored.

[3]MDLs were determined from analysis of seven undigested aqueous sample aliquots.

n.a. - Not applicable. Total recoverable digestion not suitable for organo-mercury compounds.

TABLE 8: ACCEPTANCE LIMITS FOR QC CHECK SAMPLE

METHOD PERFORMANCE (µg/L)[1]

Element	QC Check Sample Conc.	Average Recovery	Standard Deviation[2] (S_r)	Acceptance Limits[3] µg/L
Aluminum	100	100.4	5.49	84-117
Antimony	100	99.9	2.40	93-107
Arsenic	100	101.6	3.66	91-113
Barium	100	99.7	2.64	92-108
Beryllium	100	105.9	4.13	88-112[4]
Cadmium	100	100.8	2.32	94-108
Chromium	100	102.3	3.91	91-114
Cobalt	100	97.7	2.66	90-106
Copper	100	100.3	2.11	94-107
Lead	100	104.0	3.42	94-114
Manganese	100	98.3	2.71	90-106
Molybdenum	100	101.0	2.21	94-108
Nickel	100	100.1	2.10	94-106
Selenium	100	103.5	5.67	86-121
Silver	100	101.1	3.29	91-111[5]
Thallium	100	98.5	2.79	90-107
Thorium	100	101.4	2.60	94-109
Uranium	100	102.6	2.82	94-111
Vanadium	100	100.3	3.26	90-110
Zinc	100	105.1	4.57	91-119

[1]Method performance characteristics calculated using regression equations from collaborative study, Reference 11.

[2]Single-analyst standard deviation, S_r.

[3]Acceptance limits calculated as average recovery ± three standard deviations.

[4]Acceptance limits centered at 100% recovery.

[5]Statistics estimated from summary statistics at 48 and 64 µg/L.

TABLE 9: PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES

DRINKING WATER

Element	Sample Conc. µg/L	Low Spike µg/L	Average Recovery R (%)	S (R)	RPD	High Spike µg/L	Average Recovery R (%)	S (R)	RPD
Al	175	50	115.8	5.9	0.4	200	102.7	1.6	1.1
Sb	<0.4	10	99.1	0.7	2.0	100	100.8	0.7	2.0
As	<1.4	50	99.7	0.8	2.2	200	102.5	1.1	2.9
Ba	43.8	50	94.8	3.9	5.8	200	95.6	0.8	1.7
Be	<0.3	10	113.5	0.4	0.9	100	111.0	0.7	1.8
Cd	<0.5	10	97.0	2.8	8.3	100	101.5	0.4	1.0
Cr	<0.9	10	111.0	3.5	9.0	100	99.5	0.1	0.2
Co	0.11	10	94.4	0.4	1.1	100	93.6	0.5	1.4
Cu	3.6	10	101.8	8.8	17.4	100	91.6	0.3	0.3
Pb	0.87	10	97.8	2.0	2.8	100	99.0	0.8	2.2
Mn	0.96	10	96.9	1.8	4.7	100	95.8	0.6	1.8
Mo	1.9	10	99.4	1.6	3.4	100	98.6	0.4	1.0
Ni	1.9	10	100.2	5.7	13.5	100	95.2	0.5	1.3
Se	<7.9	50	99.0	1.8	5.3	200	93.5	3.5	10.7
Ag	<0.1	50	100.7	1.5	4.2	200	99.0	0.4	1.0
Tl	<0.3	10	97.5	0.4	1.0	100	98.5	1.7	4.9
Th	<0.1	10	109.0	0.7	1.8	100	106.0	1.4	3.8
U	0.23	10	110.7	1.4	3.5	100	107.8	0.7	1.9
V	<2.5	50	101.4	0.1	0.4	200	97.5	0.7	2.1
Zn	5.2	50	103.4	3.3	7.7	200	96.4	0.5	1.0

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

TABLE 9: PRECISION AND RECOVERY DATA IN AQUEOUS MATRICES (Cont'd)

WELL WATER

Element	Sample Conc. µg/L	Low Spike µg/L	Average Recovery R (%)	S (R)	RPD	High Spike µg/L	Average Recovery R (%)	S (R)	RPD
Al	34.3	50	100.1	3.9	0.8	200	102.6	1.1	1.3
Sb	0.46	10	98.4	0.9	1.9	100	102.5	0.7	1.9
As	<1.4	50	110.0	6.4	16.4	200	101.3	0.2	0.5
Ba	106	50	95.4	3.9	3.3	200	104.9	1.0	1.6
Be	<0.3	10	104.5	0.4	1.0	100	101.4	1.2	3.3
Cd	106	10	88.6	1.7	3.8	100	98.6	0.6	1.6
Cr	<0.9	10	111.0	0.0	0.0	100	103.5	0.4	1.0
Co	2.4	10	100.6	1.0	1.6	100	104.1	0.4	0.9
Cu	37.4	10	104.3	5.1	1.5	100	100.6	0.8	1.5
Pb	3.5	10	95.2	2.5	1.5	100	99.5	1.4	3.9
Mn	2770	10	*	*	1.8	100	*	*	0.7
Mo	2.1	10	103.8	1.1	1.6	100	102.9	0.7	1.9
Ni	11.4	10	116.5	6.3	6.5	100	99.6	0.3	0.0
Se	<7.9	50	127.3	8.4	18.7	200	101.3	0.2	0.5
Ag	<0.1	50	99.2	0.4	1.0	200	101.5	1.4	3.9
Tl	<0.3	10	93.9	0.1	0.0	100	100.4	1.8	5.0
Th	<0.1	10	103.0	0.7	1.9	100	104.5	1.8	4.8
U	1.8	10	106.0	1.1	1.6	100	109.7	2.5	6.3
V	<2.5	50	105.3	0.8	2.1	200	105.8	0.2	0.5
Zn	554	50	*	*	1.2	200	102.1	5.5	3.2

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

POND WATER

Element	Sample Conc. µg/L	Low Spike µg/L	Average Recovery R (%)	S (R)	RPD	High Spike µg/L	Average Recovery R (%)	S (R)	RPD
Al	610	50	*	*	1.7	200	78.2	9.2	5.5
Sb	<0.4	10	101.1	1.1	2.9	100	101.5	3.0	8.4
As	<1.4	50	100.8	2.0	5.6	200	96.8	0.9	2.6
Ba	28.7	50	102.1	1.8	2.4	200	102.9	3.7	9.0
Be	<0.3	10	109.1	0.4	0.9	100	114.4	3.9	9.6
Cd	<0.5	10	106.6	3.2	8.3	100	105.8	2.8	7.6
Cr	2.0	10	107.0	1.0	1.6	100	100.0	1.4	3.9
Co	0.79	10	101.6	1.1	2.7	100	101.7	1.8	4.9
Cu	5.4	10	107.5	1.4	1.9	100	98.1	2.5	6.8
Pb	1.9	10	108.4	1.5	3.2	100	106.1	0.0	0.0
Mn	617	10	*	*	1.1	100	139.0	11.1	4.0
Mo	0.98	10	104.2	1.4	3.5	100	104.0	2.1	5.7
Ni	2.5	10	102.0	2.3	4.7	100	102.5	2.1	5.7
Se	<7.9	50	102.7	5.6	15.4	200	105.5	1.4	3.8
Ag	0.12	50	102.5	0.8	2.1	200	105.2	2.7	7.1
Tl	<0.3	10	108.5	3.2	8.3	100	105.0	2.8	7.6
Th	0.19	10	93.1	3.5	10.5	100	93.9	1.6	4.8
U	0.30	10	107.0	2.8	7.3	100	107.2	1.8	4.7
V	3.5	50	96.1	5.2	14.2	200	101.5	0.2	0.5
Zn	6.8	50	99.8	1.7	3.7	200	100.1	2.8	7.7

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

SEWAGE TREATMENT PRIMARY EFFLUENT

Element	Sample Conc. µg/L	Low Spike µg/L	Average Recovery R (%)	S (R)	RPD	High Spike µg/L	Average Recovery R (%)	S (R)	RPD
Al	1150	50	*	*	3.5	200	100.0	13.8	1.5
Sb	1.5	10	95.7	0.4	0.9	100	104.5	0.7	1.9
As	<1.4	50	104.2	4.5	12.3	200	101.5	0.7	2.0
Ba	202	50	79.2	9.9	2.5	200	108.6	4.6	5.5
Be	<0.3	10	110.5	1.8	4.5	100	106.4	0.4	0.9
Cd	9.2	10	101.2	1.3	0.0	100	102.3	0.4	0.9
Cr	128	10	*	*	1.5	100	102.1	1.7	0.4
Co	13.4	10	95.1	2.7	2.2	100	99.1	1.1	2.7
Cu	171	10	*	*	2.4	100	105.2	7.1	0.7
Pb	17.8	10	95.7	3.8	1.1	100	102.7	1.1	2.5
Mn	199	10	*	*	1.5	100	103.4	2.1	0.7
Mo	136	10	*	*	1.4	100	105.7	2.4	2.1
Ni	84.0	10	88.4	16.3	4.1	100	98.0	0.9	0.0
Se	<7.9	50	112.0	10.9	27.5	200	108.8	3.0	7.8
Ag	10.9	50	97.1	0.7	1.5	200	102.6	1.4	3.7
Tl	<0.3	10	97.5	0.4	1.0	100	102.0	0.0	0.0
Th	0.11	10	15.4	1.8	30.3	100	29.3	0.8	8.2
U	0.71	10	109.4	1.8	4.3	100	109.3	0.7	1.8
V	<2.5	50	90.9	0.9	0.6	200	99.4	2.1	6.0
Zn	163	50	85.8	3.3	0.5	200	102.0	1.5	1.9

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

INDUSTRIAL EFFLUENT

Element	Sample Conc. µg/L	Low Spike µg/L	Average Recovery R (%)	S (R)	RPD	High Spike µg/L	Average Recovery R (%)	S (R)	RPD
Al	44.7	50	98.8	8.7	5.7	200	90.4	2.1	2.2
Sb	2990	10	*	*	0.3	100	*	*	0.0
As	<1.4	50	75.1	1.8	6.7	200	75.0	0.0	0.0
Ba	100	50	96.7	5.5	3.4	200	102.9	1.1	0.7
Be	<0.3	10	103.5	1.8	4.8	100	100.0	0.0	0.0
Cd	10.1	10	106.5	4.4	2.4	100	97.4	1.1	2.8
Cr	171	10	*	*	0.0	100	127.7	2.4	1.7
Co	1.3	10	90.5	3.2	8.7	100	90.5	0.4	1.3
Cu	101	10	*	*	0.9	100	92.5	2.0	1.6
Pb	294	10	*	*	2.6	100	108.4	2.1	0.0
Mn	154	10	*	*	2.8	100	103.6	3.7	1.6
Mo	1370	10	*	*	1.4	100	*	*	0.7
Ni	17.3	10	107.4	7.4	5.0	100	88.2	0.7	1.0
Se	15.0	50	129.5	9.3	15.1	200	118.3	1.9	3.6
Ag	<0.1	50	91.8	0.6	1.7	200	87.0	4.9	16.1
Tl	<0.3	10	90.5	1.8	5.5	100	98.3	1.0	2.8
Th	0.29	10	109.6	1.2	2.7	100	108.7	0.0	0.0
U	0.17	10	104.8	2.5	6.6	100	109.3	0.4	0.9
V	<2.5	50	74.9	0.1	0.3	200	72.0	0.0	0.0
Zn	43.4	50	85.0	4.0	0.6	200	97.6	1.0	0.4

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 10: PRECISION AND RECOVERY DATA IN SOLID MATRICES

EPA HAZARDOUS SOIL #884

Element	Sample Conc. (mg/kg)	Low+ Spike (mg/kg)	Average Recovery R (%)	S (R)	RPD	High+ Spike (mg/kg)	Average Recovery R (%)	S (R)	RPD
Al	5170	20	*	*	–	100	*	*	–
Sb	5.4	20	69.8	2.5	4.7	100	70.4	1.8	6.5
As	8.8	20	104.7	5.4	9.1	100	102.2	2.2	5.4
Ba	113	20	54.9	63.6	18.6	100	91.0	9.8	0.5
Be	0.6	20	100.1	0.6	1.5	100	102.9	0.4	1.0
Cd	1.8	20	97.3	1.0	1.4	100	101.7	0.4	1.0
Cr	83.5	20	86.7	16.1	8.3	100	105.5	1.3	0.0
Co	7.1	20	98.8	1.2	1.9	100	102.9	0.7	1.8
Cu	115	20	86.3	13.8	3.4	100	151.7	4.2	4.6
Pb	152	20	85.0	45.0	13.9	100	85.2	25.7	23.7
Mn	370	20	*	*	12.7	100	95.2	10.4	2.2
Mo	4.8	20	95.4	1.5	2.9	100	102.3	0.7	2.0
Ni	19.2	20	101.7	3.8	1.0	100	100.7	0.8	0.8
Se	<3.2	20	79.5	7.4	26.4	100	94.8	9.4	26.5
Ag	1.1	20	96.1	0.6	0.5	100	97.9	0.8	2.3
Tl	0.24	20	94.3	1.1	3.1	100	76.0	1.0	2.9
Th	1.0	20	69.8	0.6	1.3	100	102.9	2.2	7.9
U	1.1	20	100.1	0.2	0.0	100	106.7	0.0	0.0
V	17.8	20	109.2	4.2	2.3	100	113.4	1.3	2.4
Zn	128	20	87.0	27.7	5.5	100		12.9	14.1

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 determined.
+ Equivalent.

TABLE 10: PRECISION AND RECOVERY DATA IN SOLID MATRICES

NBS 1645 RIVER SEDIMENT

Element	Sample Conc. (mg/kg)	Low[+] Spike (mg/kg)	Average Recovery R (%)	S (R)	RPD	High[+] Spike (mg/kg)	Average Recovery R (%)	S (R)	RPD
Al	5060	20	*	*	–	100	*	*	–
Sb	21.8	20	73.9	6.5	9.3	100	81.2	1.5	3.9
As	67.2	20	104.3	13.0	7.6	100	107.3	2.1	2.9
Ba	54.4	20	105.6	4.9	2.8	100	98.6	2.2	3.9
Be	0.59	20	88.8	0.2	0.5	100	87.9	0.1	0.2
Cd	8.3	20	92.9	0.4	0.0	100	95.7	1.4	3.9
Cr	29100	20	*	*	–	100	*	*	–
Co	7.9	20	97.6	1.3	2.6	100	103.1	0.0	0.0
Cu	112	20	121.0	9.1	1.5	100	105.2	2.2	1.8
Pb	742	20	*	*	–	100	–	–	–
Mn	717	20	*	*	–	100	–	–	–
Mo	17.1	20	89.8	8.1	12.0	100	98.4	0.7	0.9
Ni	41.8	20	103.7	6.5	4.8	100	102.2	0.8	0.0
Se	<3.2	20	108.3	14.3	37.4	100	93.9	5.0	15.1
Ag	1.8	20	94.8	1.6	4.3	100	96.2	0.7	1.9
Tl	1.2	20	91.2	1.3	3.6	100	94.4	0.4	1.3
Th	0.90	20	91.3	0.9	2.6	100	92.3	0.9	2.8
U	0.79	20	95.6	1.8	5.0	100	98.5	1.2	3.5
V	21.8	20	91.8	4.6	5.7	100	100.7	0.6	0.8
Zn	1780	20	*	*	–	100	*	*	–

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 determined.
[+] Equivalent.

TABLE 10: PRECISION AND RECOVERY DATA IN SOLID MATRICES

EPA ELECTROPLATING SLUDGE #286

Element	Sample Conc. (mg/kg)	Low+ Spike (mg/kg)	Average Recovery R (%)	S (R)	RPD	High+ Spike (mg/kg)	Average Recovery R (%)	S (R)	RPD
Al	5110	20	*	*	–	100	*	*	–
Sb	8.4	20	55.4	1.5	4.1	100	61.0	0.2	0.9
As	41.8	20	91.0	2.3	1.7	100	94.2	0.8	1.5
Ba	27.3	20	1.8	7.1	8.3	100	0	1.5	10.0
Be	0.25	20	92.0	0.9	2.7	100	93.4	0.3	0.9
Cd	112	20	85.0	5.2	1.6	100	88.5	0.8	0.5
Cr	7980	20	*	*	–	100	*	*	–
Co	4.1	20	89.2	1.8	4.6	100	88.7	1.5	4.6
Cu	740	20	*	*	6.0	100	61.7	20.4	5.4
Pb	1480	20	*	*	–	100	*	*	–
Mn	295	20	*	*	–	100	–	–	–
Mo	13.3	20	82.9	1.2	1.3	100	89.2	0.4	1.0
Ni	450	20	*	*	6.8	100	83.0	10.0	4.5
Se	3.5	20	89.7	3.7	4.2	100	91.0	6.0	18.0
Ag	5.9	20	89.8	2.1	4.6	100	85.1	0.4	1.1
Tl	1.9	20	96.9	0.9	2.4	100	98.9	0.9	2.4
Th	3.6	20	91.5	1.3	3.2	100	97.4	0.7	2.0
U	2.4	20	107.7	2.0	4.6	100	109.6	0.7	1.8
V	21.1	20	105.6	1.8	2.1	100	97.4	1.1	2.5
Zn	13300	20	*	*	–	100	*	*	–

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 determined.
+ Equivalent.

TABLE 11: PRIMARY DRINKING WATER CONTAMINANTS
PRECISION AND RECOVERY DATA

Analyte	Regional Sample Background Concentration, µg/L (IV)	(VI)	(X)	Average Mean[1] % Recovery	S (R)
Antimony	0.16	0.07	0.03	114%	1.9
Arsenic	< MDL	2.4	1.0	93	8.5
Barium	4.6	280	14.3	(*)	–
Beryllium	< MDL	< MDL	< MDL	100%	8.2
Cadmium	0.05	0.05	0.03	81	4.0
Chromium	0.71	5.1	0.10	94	2.5
Copper	208	130	14.3	(*)	–
Lead	1.2	1.2	2.5	91	2.6
Mercury	< MDL	0.23	< MDL	86	11.4
Nickel	1.7	3.6	0.52	101%	11.5
Selenium	< MDL	4.3	< MDL	98	8.4
Thallium	< MDL	0.01	< MDL	100	1.4

[1]The three regional waters were fortified with 1.0 µg/L of all analytes listed, except selenium, which was fortified to 20 µg/L.

(*) Recovery of barium and copper was not calculated because the analyte addition was <20% the sample background concentration in all waters. (Recovery calculations are not required if the concentration of the analyte added is less than 30% of the sample background concentration. Section 9.4.3).

S (R) Standard deviation of the mean percent recoveries.

TABLE 12: SUMMARY STATISTICS AND DESCRIPTIVE EQUATIONS FOR THE 20 ANALYTES TESTED IN THE COLLABORATIVE STUDY

		Reagent Water				Finished Drinking Water				Ground Water			
Analyte	C[a]	$\bar{X}$[b]	S_R	S_r	Regr. Equations	$\bar{X}$	S_R	S_r	Regr. Equations	$\bar{X}$	S_R	S_r	Regr. Equations
Aluminum	8.00	10.01	2.33	1.74	$\bar{X} = 0.992C + 1.19$	11.18	9.02	6.34	$\bar{X} = 0.954C + 2.38$	9.86	7.10	2.70	$\bar{X} = 0.946C + 2.20$
	12.00	10.98	5.16		$S_R = 0.056\bar{X} + 2.59$[c]	11.02	3.02		$S_R = 7.70$[d]	13.40	10.27		$S_R = 0.169\bar{X} + 6.22$[c]
	56.00	59.13	5.55	4.19	$S_r = 0.042\bar{X} + 1.27$	56.97	7.14	6.18	$S_r = 0.013\bar{X} + 6.17$	51.75	10.78	16.92	$S_r = 0.172\bar{X} + 0.75$[c]
	80.00	82.59	4.92			82.73	8.01			82.83	33.37		
	160.00	158.95	11.82	8.90		159.89	11.94	10.59		155.40	15.39	19.27	
	200.00	200.89	8.61			189.98	12.97			189.64	31.46		
Antimony	2.80	2.75	0.27	0.27	$\bar{X} = 0.999C + 0.04$	2.73	0.29	0.17	$\bar{X} = 0.983C + 0.03$	2.82	0.19	0.22	$\bar{X} = 1.003C + 0.01$
	4.00	4.22	0.46		$S_R = 0.013\bar{X} + 0.61$[e]	4.10	0.47		$S_R = 0.049\bar{X} + 0.19$	4.02	0.35		$S_R = 0.059\bar{X} + 0.04$
	20.00	19.76	1.09	0.85	$S_r = 0.022\bar{X} + 0.20$	19.17	1.37	0.66	$S_r = 0.026\bar{X} + 0.08$	20.12	0.82	0.97	$S_r = 0.058\bar{X} + 0.02$
	28.00	27.48	1.38			26.48	1.72			27.77	1.38		
	80.00	82.52	2.24	1.76		83.43	2.05	2.46		80.34	9.14	6.80	
	100.00	98.06	1.34			97.19	5.31			101.09	2.89		
Arsenic	8.00	8.64	3.01	3.02	$\bar{X} = 1.013C + 0.50$	9.00	3.13	1.96	$\bar{X} = 0.993C + 0.57$	10.40	5.17	4.90	$\bar{X} = 0.949C + 0.91$
	12.00	12.58	3.18		$S_R = 0.031\bar{X} + 2.74$	11.37	1.77		$S_R = 0.018\bar{X} + 2.55$	7.85	4.62		$S_R = 0.048\bar{X} + 4.52$
	56.00	55.44	4.64	3.51	$S_r = 0.007\bar{X} + 2.95$	53.77	4.12	4.07	$S_r = 0.031\bar{X} + 1.65$	53.25	3.49	7.88	$S_r = 0.059\bar{X} + 4.29$
	80.00	85.15	2.54			87.72	4.14			83.60	12.46		
	160.00	161.80	11.15	3.96		157.56	4.83	6.30		159.86	11.67	14.94	
	200.00	201.52	10.81			197.99	10.66			194.41	18.24		
Barium	8.01	7.58	0.50	0.48	$\bar{X} = 1.001C - 0.36$	8.21	1.21	1.11	$\bar{X} = 0.995C + 0.37$	8.04	2.60	2.24	$\bar{X} = 1.055C - 0.21$
	12.00	11.81	1.05		$S_R = 0.039\bar{X} + 0.31$	12.56	1.79		$S_R = 0.045\bar{X} + 0.97$[c]	12.85	1.45		$S_R = 0.020\bar{X} + 2.05$
	48.00	47.32	1.60	1.82	$S_r = 0.024\bar{X} + 0.25$	49.13	3.72	3.77	$S_r = 0.040\bar{X} + 0.72$[c]	50.12	2.98	2.19	$S_r = 0.014\bar{X} + 2.08$
	64.00	65.52	2.90			65.30	4.16			69.53	2.66		
	160.00	157.09	6.53	4.07		155.25	7.82	5.67		164.44	8.81	6.61	
	200.00	198.53	8.28			196.52	5.70			208.32	9.22		
Beryllium	2.80	3.31	0.81	0.26	$\bar{X} = 1.056C + 0.32$	3.15	0.47	0.31	$\bar{X} = 1.055C + 0.20$	3.02	0.46	0.22	$\bar{X} = 1.049C + 0.08$
	4.00	4.45	0.73		$S_R = 0.067\bar{X} + 0.55$	4.45	0.51		$S_R = 0.057\bar{X} + 0.28$	4.27	0.44		$S_R = 0.084\bar{X} + 0.16$
	20.00	22.38	2.76	1.00	$S_r = 0.038\bar{X} + 0.11$	21.27	1.23	0.63	$S_r = 0.016\bar{X} + 0.25$	21.55	1.72	1.10	$S_r = 0.043\bar{X} + 0.06$
	28.00	30.02	2.86			29.57	1.67			29.24	2.09		
	80.00	84.18	4.79	4.02		87.59	6.89	1.88		84.23	9.05	4.32	
	100.00	102.88	5.90			102.64	6.27			103.39	10.17		
Cadmium	4.00	4.01	0.34	0.20	$\bar{X} = 1.007C + 0.07$	4.11	0.88	0.71	$\bar{X} = 0.985C + 0.10$	3.98	0.48	0.14	$\bar{X} = 0.944C + 0.11$
	6.00	6.32	0.49		$S_R = 0.041\bar{X} + 0.19$	5.87	0.58		$S_R = 0.031\bar{X} + 0.65$	5.62	0.73		$S_R = 0.017\bar{X} + 1.09$[e]
	20.00	19.81	1.12	0.86	$S_r = 0.022\bar{X} + 0.10$[c]	19.57	1.45	1.26	$S_r = 0.021\bar{X} + 0.61$	18.15	1.73	0.88	$S_r = 0.029\bar{X} + 0.01$
	28.00	28.33	0.94			27.68	1.27			26.86	2.59		
	80.00	81.28	4.91	1.33		80.62	4.45	2.02		77.83	3.05	1.88	
	100.00	100.11	3.24			98.15	3.60			95.31	2.04		

TABLE 12: SUMMARY STATISTICS AND DESCRIPTIVE EQUATIONS FOR THE 20 ANALYTES TESTED IN THE COLLABORATIVE STUDY

		Reagent Water				Finished Drinking Water				Ground Water			
Analyte	C[a]	$\bar{X}$[b]	S_R	S_r	Regr. Equations	$\bar{X}$	S_R	S_r	Regr. Equations	$\bar{X}$	S_R	S_r	Regr. Equations
Chromium	8.00	8.27	0.32	1.54	$\bar{X} = 1.017\bar{C} + 0.62$	9.46	2.34	2.08	$\bar{X} = 0.990\bar{C} + 1.45$	8.98	1.47	0.37	$\bar{X} = 1.026\bar{C} + 0.89$
	12.00	13.88	3.10		$S_R = 0.066\bar{X} + 0.48$	13.10	2.39		$S_R = 0.015\bar{X} + 2.19$	13.42	1.13		$S_R = 0.067\bar{X}$ 0.68
	56.00	57.86	4.03	2.68	$S_r = 0.026\bar{X} + 1.25$	56.04	2.24	1.29	$S_r = 2.18$[d]	59.35	5.99	5.42	$S_r = 0.068\bar{X} - 0.37$
	80.00	84.73	2.65			84.38	3.18			83.90	5.70		
	160.00	157.66	13.62	6.97		158.24	5.12	3.16		164.58	14.11	9.80	
	200.00	197.43	9.47			196.72	7.47			199.88	11.19		
Cobalt	0.80	0.88	0.10	0.05	$\bar{X} = 0.977\bar{C} + 0.01$	0.92	0.45	0.31	$\bar{X} = 0.964\bar{C} + 0.06$	0.85	0.13	0.09	$\bar{X} = 0.989\bar{C} - 0.01$
	1.21	0.98	0.04		$S_R = 0.028\bar{X} + 0.06$	1.02	0.10		$S_R = 0.019\bar{X} + 0.32$	1.04	0.18		$S_R = 0.057\bar{X} + 0.09$
	20.10	20.77	0.74	0.67	$S_r = 0.027\bar{X} + 0.02$	20.45	0.91	0.53	$S_r = 0.014\bar{X} + 0.30$	20.81	1.11	1.12	$S_r = 0.012\bar{X} + 0.40$[e]
	28.20	27.75	0.96			27.29	1.22			28.07	2.16		
	80.50	78.59	2.29	2.31		78.04	3.72	1.84		79.26	4.66	1.34	
	101.00	98.79	2.94			97.62	4.62			99.41	4.22		
Copper	4.00	3.88	0.73	0.59	$\bar{X} = 1.003\bar{C} - 0.05$	3.33	0.85	0.99	$\bar{X} = 0.976\bar{C} - 0.38$	3.86	1.40	0.71	$\bar{X} = 0.977\bar{C} - 0.01$
	6.00	6.14	1.00		$S_R = 0.037\bar{X} + 0.64$	5.95	1.78		$S_R = 0.063\bar{X} + 0.86$	5.96	0.95		$S_R = 0.073\bar{X} + 0.92$
	20.00	20.07	1.08	0.92	$S_r = 0.016\bar{X} + 0.51$	18.90	1.64	1.51	$S_r = 0.029\bar{X} + 0.86$	18.97	1.68	2.32	$S_r = 0.077\bar{X} + 0.35$
	28.00	27.97	1.94			27.21	2.76			27.44	2.58		
	80.00	79.80	3.22	1.91		76.64	5.30	3.42		79.30	9.05	6.54	
	100.00	99.57	4.42			96.17	5.64			97.54	11.16		
Lead	4.00	4.00	1.57	1.62	$\bar{X} = 1.043\bar{C} - 0.31$	3.44	1.15	1.18	$\bar{X} = 1.032\bar{C} - 0.30$	4.20	1.13	1.76	$\bar{X} = 1.012\bar{C} + 0.15$
	6.00	5.56	2.00		$S_R = 0.064\bar{X} + 1.43$[c]	6.84	1.10		$S_R = 0.015\bar{X} + 1.06$	6.27	2.38		$S_R = 0.048\bar{X} + 1.27$
	20.00	20.54	2.91	4.36	$S_r = 3.42$[d]	20.18	1.20	1.44	$S_r = 0.011\bar{X} + 1.13$	19.57	2.72	0.88	$S_r = 1.78$[d]
	28.00	30.90	4.58			28.08	1.57			28.55	1.73		
	80.00	80.57	3.13	4.29		80.92	2.30	2.07		82.47	4.38	2.69	
	100.00	102.93	6.62			101.60	3.23			102.47	3.58		
Manganese	0.80	0.86	0.15	0.09	$\bar{X} = 0.983\bar{C} + 0.02$	0.96	0.32	0.42	$\bar{X} = 0.989\bar{C} + 0.10$	0.64	0.22	0.17	$\bar{X} = 0.954\bar{C} - 0.16$
	1.20	1.09	0.12		$S_R = 0.026\bar{X} + 0.11$	1.13	0.38		$S_R = 0.047\bar{X} + 0.29$	0.90	0.21		$S_R = 0.103\bar{X} + 0.14$
	20.00	20.43	0.89	0.72	$S_r = 0.027\bar{X} + 0.06$	21.06	1.32	0.96	$S_r = 0.021\bar{X} + 0.40$	19.61	2.60	2.62	$S_r = 0.025\bar{X} + 0.09$[e]
	28.00	27.53	0.41			27.60	1.47			25.65	4.10		
	80.00	79.00	3.16	2.38		79.57	4.18	2.01		77.38	6.13	2.90	
	100.00	97.60	2.51			97.97	4.10			95.86	6.74		

TABLE 12: SUMMARY STATISTICS AND DESCRIPTIVE EQUATIONS FOR THE 20 ANALYTES TESTED IN THE COLLABORATIVE STUDY

		Reagent Water				Finished Drinking Water				Ground Water			
Analyte	C[a]	$\bar{X}$[b]	S_R	S_r	Regr. Equations	$\bar{X}$	S_R	S_r	Regr. Equations	$\bar{X}$	S_R	S_r	Regr. Equations
Molybdenum	2.80	2.63	0.32	0.16	$\bar{X} = 1.012C - 0.20$	2.80	0.20	0.32	$\bar{X} = 1.013C - 0.07$	3.00	0.47	0.42	$\bar{X} = 1.032C - 0.09$
	4.00	3.85	0.31		$S_R = 0.032\bar{X} + 0.22$	3.95	0.47		$S_R = 0.037\bar{X} + 0.17$	3.60	0.90		$S_R = 0.55\bar{X} + 0.43$
	20.00	19.75	0.64	0.64	$S_r = 0.021X + 0.09$	19.78	0.60	1.16	$S_r = 0.035X + 0.20$	20.69	1.37	1.11	$S_r = 0.042X + 0.27$
	28.00	27.87	1.07			27.87	1.51			28.80	2.01		
	80.00	83.07	3.07	1.78		85.65	3.50	3.07		84.26	4.13	4.81	
	100.00	100.08	4.32			99.06	2.89			103.57	6.10		
Nickel	4.00	4.02	0.41	0.50	$\bar{X} = 1.000C + 0.12$	3.66	0.53	1.03	$\bar{X} = 0.953C - 0.19$	4.81	2.06	2.82	$\bar{X} = 1.022C + 0.66$
	6.00	6.36	0.91		$S_R = 0.051\bar{X} + 0.31$	5.44	1.32		$S_R = 0.046\bar{X} + 0.56$	6.67	3.66		$S_R = 0.091\bar{X} + 2.03$
	20.00	19.93	1.30	0.63	$S_r = 0.017X + 0.40$	18.42	0.87	1.11	$S_r = 0.023X + 0.91$	20.58	3.71	2.37	$S_r = 0.008X + 2.75$[c]
	28.00	28.02	1.25			27.09	1.68			30.73	3.75		
	80.00	79.29	2.95	2.55		75.84	4.40	3.94		82.71	9.49	5.42	
	100.00	100.87	7.20			95.83	4.41			101.00	9.89		
Selenium	32.00	33.54	4.63	1.57	$\bar{X} = 1.036C - 0.06$	32.57	4.37	3.65	$\bar{X} = 1.022C + 0.14$	32.46	4.95	3.24	$\bar{X} = 1.045C - 0.83$
	40.00	41.03	6.04		$S_R = 0.051\bar{X} + 3.24$	42.18	3.71		$S_R = 0.056\bar{X} + 2.10$	41.46	3.30		$S_R = 0.037\bar{X} + 2.97$
	80.00	81.40	5.86	5.44	$S_r = 0.061X - 0.64$	79.97	6.66	5.28	$S_r = 0.040X + 2.15$	81.63	6.94	5.65	$S_r = 0.058X + 1.02$
	96.10	98.34	8.57			94.94	7.90			98.92	4.39		
	160.00	163.58	15.69	9.86		163.48	9.17	10.06		167.54	8.69	12.98	
	200.00	214.30	10.57			212.19	16.49			209.21	14.65		
Silver	0.80	0.93	0.09	0.14	$\bar{X} = 0.917C + 0.26$	0.70	0.34	0.34	$\bar{X} = 0.888C + 0.09$	0.70	0.26	0.10	$\bar{X} = 0.858C - 0.00$
	1.20	1.51	0.23		$S_R = 0.196\bar{X} - 0.09$	1.37	0.33		$S_R = 0.186\bar{X} + 0.17$	0.98	0.28		$S_R = 0.169\bar{X} + 0.14$
	48.00	49.39	3.25	1.81	$S_r = 0.053X + 0.08$	45.43	6.78	5.15	$S_r = 0.164X + 0.18$	45.59	4.27	2.70	$S_r = 0.120X - 0.01$
	64.00	63.54	2.75			60.35	2.22			59.71	6.58		
	160.00	136.42	48.31	12.19		119.06	55.28	36.34		121.43	42.55	28.19	
	200.00	153.74	57.34			172.15	31.92			160.69	27.15		
Thallium	2.80	2.89	0.23	0.22	$\bar{X} = 0.984\bar{X} + 0.08$	2.88	0.40	0.16	$\bar{X} = 1.010C + 0.01$	2.88	0.14	0.12	$\bar{X} = 1.023C - 0.06$
	4.00	3.92	0.15		$S_R = 0.035\bar{X} + 0.09$	3.96	0.21		$S_R = 0.040\bar{X} + 0.21$	3.88	0.37		$S_R = 0.056\bar{X} + 0.04$
	20.00	19.27	0.99	0.67	$S_r = 0.027X + 0.13$	19.77	1.13	0.83	$S_r = 0.039X + 0.02$	20.22	1.05	0.65	$S_r = 0.049X - 0.06$
	28.00	28.08	0.83			27.61	1.24			28.65	1.50		
	80.00	81.29	3.65	2.86		85.32	4.08	4.05		83.97	6.10	6.05	
	100.00	96.69	2.86			100.07	4.33			101.09	4.15		
Thorium	0.80	0.93	0.16	0.09	$\bar{X} = 1.013C + 0.08$	0.78	0.13	0.07	$\bar{X} = 1.019C - 0.06$	0.87	0.17	0.07	$\bar{X} = 1.069C - 0.03$
	1.20	1.22	0.19		$S_R = 0.036\bar{X} + 0.13$	1.09	0.19		$S_R = 0.035\bar{X} + 0.12$	1.15	0.17		$S_R = 0.041\bar{X} + 0.13$
	20.00	20.88	0.90	0.71	$S_r = 0.025X + 0.07$	21.66	0.94	0.54	$S_r = 0.024X + 0.05$	21.78	0.90	0.94	$S_r = 0.027X + 0.04$
	28.00	27.97	1.11			28.09	0.83			29.86	1.65		
	80.10	81.14	2.99	2.14		79.99	2.03	2.60		86.00	3.43	1.95	
	100.00	102.64	3.39			100.50	4.56			107.35	4.72		

TABLE 12: SUMMARY STATISTICS AND DESCRIPTIVE EQUATIONS FOR THE 20 ANALYTES TESTED IN THE COLLABORATIVE STUDY

		Reagent Water				Finished Drinking Water				Ground Water			
Analyte	C[a]	$\bar{X}$[b]	S_R	S_r	Regr. Equations	$\bar{X}$	S_R	S_r	Regr. Equations	$\bar{X}$	S_R	S_r	Regr. Equations
Uranium	0.80	0.86	0.05	0.08	$\bar{X} = 1.026\underline{C} - 0.02$	0.85	0.15	0.09	$\bar{X} = 1.026\underline{C} - 0.04$	0.84	0.23	0.19	$\bar{X} = 1.058\underline{C} - 0.06$
	1.20	1.10	0.11		$S_R = 0.048\bar{X} + 0.02$	1.05	0.13		$S_R = 0.044\bar{X} + 0.11$	1.10	0.14		$S_R = 0.039\bar{X} + 0.17$
	20.10	21.38	0.99	0.82	$S_r = 0.027\bar{X} + 0.05$	22.30	1.40	0.46	$S_r = 0.022\bar{X} + 0.07$	21.56	1.11	1.08	$S_r = 0.028\bar{X} + 0.16$
	28.10	28.36	1.10			28.89	1.47			29.86	1.83		
	80.30	82.47	4.03	2.16		80.31	2.00	2.71		85.01	3.76	2.00	
	100.00	103.49	5.24			100.70	5.30			106.47	3.74		
Vanadium	32.00	31.02	2.68	2.19	$\bar{X} = 1.025C - 2.21$	33.15	2.51	2.28	$\bar{X} = 1.022\underline{C} - 0.30$	33.25	3.83	1.87	$\bar{X} = 1.076\underline{C} - 1.87$
	40.00	38.54	2.94		$S_R = 3.79$[d]	40.20	1.88		$S_R = 0.023\bar{X} + 1.45$	40.34	3.08		$S_R = 0.033\bar{X} + 2.25$
	80.00	79.14	4.94	4.29	$S_r = 3.26$[d]	77.83	4.18	2.75	$S_r = 0.023\bar{X} + 1.38$	84.42	3.97	2.93	$S_r = 0.049\bar{X} - 0.09$
	96.00	93.47	3.85			96.32	1.34			98.70	5.03		
	160.00	162.43	5.67	3.30		161.89	7.63	6.56		170.94	9.09	11.55	
	200.00	208.20	2.65			214.91	5.89			217.90	11.36		
Zinc	8.00	8.33	2.56	1.78	$\bar{X} = 1.042\underline{C} + 0.87$	11.60	6.18	5.72	$\bar{X} = 0.943\underline{C} + 2.54$	7.29	1.12	2.20	$\bar{X} = 0.962\underline{C} + 0.07$
	12.00	15.49	4.18		$S_R = 0.041\bar{X} + 2.60$	10.21	4.96		$S_R = 0.048\bar{X} + 5.27$	12.66	3.24		$S_R = 0.093\bar{X} + 0.92$
	56.00	56.07	2.91	2.47	$S_r = 0.030\bar{X} + 1.42$	56.83	7.66	4.56	$S_r = 0.004\bar{X} + 5.66$[c]	54.86	5.12	7.24	$S_r = 0.069\bar{X} + 1.55$
	80.00	85.53	5.81			82.88	8.34			78.62	8.56		
	160.00	165.17	7.78	9.87		156.69	17.01	9.48		150.12	12.52	10.84	
	200.00	207.27	14.61			191.59	17.21			184.37	16.59		

[a] True Value for the concentration added ($\mu g/L$)
[b] Mean Recovery ($\mu g/L$)
[c] $COD_w < 0.5$ - Use of regression equation outside study concentration range not recommended.
[d] $COD_w < 0$ - Mean precision is reported.
[e] $COD_w < 0$ - Unweighted linear regression equation presented.

TABLE 13: BACKGROUND AND SPIKE MEASUREMENTS IN WASTEWATER DIGESTATE[a]

	Background		Concentrate 1					Concentrate 2					
	Conc. µg/L	Std Dev µg/L	Spike µg/L	Found µg/L	Std Dev µg/L	% Rec %	RSD %	Spike µg/L	Found µg/L	Std Dev µg/L	% Rec %	RSD %	RSD_r %
Be	0.0	0.0	100	94.5	11.8	94.5	12.5	125	118.1	14.7	94.5	12.4	3.5
Al	78.2	12.4	200	260.9	41.2	91.4	15.8	250	309.1	48.5	92.4	15.7	2.7
Cr	19.5	8.1	200	222.2	23.3	101.4	10.5	250	274.3	26.6	101.9	9.7	2.0
V	1.9	2.8	250	271.8	36.5	108.0	13.4	200	219.3	30.1	108.7	13.7	2.6
Mn	296.6	24.7	125	419.0	35.7	97.9	8.5	100	397.4	34.8	100.8	8.8	1.0
Co	2.5	0.4	125	124.7	12.3	97.8	9.9	101	100.7	9.4	97.2	9.3	2.8
Ni	47.3	5.0	125	161.7	4.9	91.5	3.0	100	142.7	5.6	95.4	3.9	2.1
cu	77.4	13.2	125	194.5	29.5	93.7	15.2	100	172.3	26.6	94.9	15.4	2.2
Zn	77.4	4.9	200	257.4	16.3	90.0	6.3	250	302.5	21.1	90.0	7.0	1.8
As	0.8	1.1	200	194.9	8.0	97.1	4.1	250	244.7	12.8	97.6	5.2	3.4
Se	4.5	6.2	250	236.8	14.2	92.9	6.0	200	194.3	9.3	94.9	4.8	3.8
Mo	166.1	9.4	100	269.8	19.0	103.7	7.0	125	302.0	18.0	108.7	6.0	1.5
Ag	0.6	0.7	200	176.0	14.6	87.7	8.3	250	214.6	17.8	85.6	8.3	2.3
Cd	2.7	1.1	125	117.0	4.8	91.4	4.1	100	96.6	3.2	93.9	3.3	2.9
Sb	3.3	0.2	100	100.2	4.8	96.9	4.8	125	125.9	4.3	98.1	3.4	1.8
Ba	68.6	3.3	250	321.0	19.4	101.0	6.0	200	279.3	17.2	105.4	6.2	2.5
Tl	0.1	0.1	100	103.3	8.0	103.2	7.7	125	129.2	8.9	103.3	6.9	2.1
Pb	6.9	0.5	125	135.1	7.8	102.6	5.8	100	110.3	6.3	103.4	5.7	1.8
Th	0.1	0.1	125	140.2	19.5	112.1	13.9	100	113.3	15.4	113.2	13.6	2.7
U	0.4	0.2	125	141.2	19.3	112.6	13.7	100	113.6	16.0	113.2	14.1	2.5

[a]Results from 10 participating laboratories. Wastewater digestate supplied with the study materials. Mean background concentrations determined by the participants.

TABLE 14: SPIKE MEASUREMENTS IN PARTICIPANTS WASTEWATER[a]

	Concentrate 1					Concentrate 2					
	Spike µg/L	Found µg/L	Std Dev µg/L	% Rec %	RSD %	Spike µg/L	Found µg/L	Std Dev µg/L	% Rec %	RSD %	RSD_r %
Be	101	103.4	12.0	103.4	11.6	125	128.2	13.6	102.6	10.6	2.4
Al	200	198.7	23.9	99.4	12.0	250	252.4	15.5	101.0	6.1	2.9
Cr	200	205.4	12.3	102.7	6.0	250	253.4	15.4	101.4	6.1	1.1
V	250	246.5	4.4	98.6	1.8	200	196.8	2.8	98.4	1.4	2.0
Mn	125	119.0	5.4	95.2	4.5	100	95.5	4.3	95.5	4.5	0.8
Co	125	125.8	7.0	100.6	5.6	101	99.5	5.3	98.5	5.3	1.8
Ni	125	127.4	9.7	101.9	7.6	100	101.0	7.5	101.0	7.4	1.7
cu	125	126.8	5.3	101.4	4.2	100	105.3	3.6	105.3	3.4	2.8
Zn	200	201.4	36.7	100.7	18.2	250	246.4	29.7	98.6	12.1	2.6
As	200	207.3	11.9	103.7	5.7	250	263.0	2.6	105.2	1.0	3.2
Se	250	256.8	26.4	102.7	10.3	200	214.0	18.7	107.3	8.7	3.6
Mo	100	98.6	4.6	98.6	4.7	125	123.2	6.7	98.6	5.4	2.2
Ag	200	200.7	48.9	100.4	24.4	250	231.2	63.5	92.5	27.5	8.2
Cd	125	123.2	11.5	98.6	9.3	100	95.8	2.9	95.8	3.0	5.8
Sb	100	92.2	4.4	92.2	4.8	125	119.0	1.0	95.2	0.8	2.8
Ba	250	245.2	12.8	98.1	5.2	200	204.7	12.1	102.4	5.9	2.1
Tl	100	100.0	0.9	100.0	0.9	125	128.0	6.0	102.4	4.7	3.5
Pb	125	125.8	5.1	100.6	4.1	100	100.8	2.7	100.8	2.7	2.2
Th	125	124.2	7.6	99.4	6.1	100	99.8	5.7	99.8	5.7	3.2
U	125	130.4	10.3	104.3	7.9	100	106.4	6.8	106.4	6.4	2.3

[a]Results from five participating laboratories. Mean concentrations before spiking are not listed because they varied considerably among the different wastewaters.

METHOD 300.0

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

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Revision 2.1
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METHOD 300.0

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method covers the determination of the following inorganic anions:

PART A.

Bromide	Nitrite
Chloride	Ortho-Phosphate-P
Fluoride	Sulfate
Nitrate	

PART B.

Bromate	Chlorite
Chlorate	

1.2 The matrices applicable to each method are shown below:

1.2.1 Drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction 11.7), leachates (when no acetic acid is used).

1.2.2 Drinking water and reagent waters

1.3 The single laboratory Method Detection Limit (MDL defined in Section 3.2) for the above analytes is listed in Tables 1A and 1B. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample.

1.4 Method A is recommended for drinking and wastewaters. The multilaboratory ranges tested for each anion are as follows:

Analyte	mg/L
Bromide	0.63 - 21.0
Chloride	0.78 - 26.0
Fluoride	0.26 - 8.49
Nitrate-N	0.42 - 14.0
Nitrite-N	0.36 - 12.0
Otho-Phosphate-P	0.69 - 23.1
Sulfate	2.85 - 95.0

1.5 This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatograms.

1.6 When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the use of a fortified sample matrix covering the anions of interest. The fortification procedure is described in Section 11.6.

1.7 Users of the method data should state the data-quality objectives prior to analysis. Users of the method must demonstrate the ability to generate acceptable results with this method, using the procedures described in Section 9.0.

2.0 SUMMARY OF METHOD

2.1 A small volume of sample, typically 2-3 mL, is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, analytical column, suppressor device, and conductivity detector.

2.2 The main differences between Parts A and B are the separator columns and guard columns. Sections 6.0 and 7.0 will elicit the differences.

2.3 An extraction procedure must be performed to use this method for solids (See Section 11.7).

2.4 Limited performance-based method modifications may be acceptable provided they are fully documented and meet or exceed requirements expressed in Section 9.0, Quality Control.

3.0 DEFINITIONS

3.1 **Calibration Blank (CB)** -- A volume of reagent water fortified with the same matrix as the calibration standards, but without the analytes, internal standards, or surrogate analytes.

3.2 **Calibration Standard (CAL)** -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.3 **Field Duplicates (FD)** -- Two separate samples collected at the same time and placed under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.4 **Instrument Performance Check Solution (IPC)** -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.5 **Laboratory Fortified Blank (LFB)** -- An aliquot of reagent water or other blank matrices 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.

3.6 **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.

3.7 **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, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.8 **Linear Calibration Range (LCR)** -- The concentration range over which the instrument response is linear.

3.9 **Material Safety Data Sheet (MSDS)** -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.10 **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.

3.11 **Performance Evaluation Sample (PE)** -- A solution of method analytes distributed by the Quality Assurance Research Division (QARD), Environmental Monitoring Systems Laboratory (EMSL-Cincinnati), U. S. Environmental Protection Agency, Cincinnati, Ohio, to multiple laboratories for analysis. A volume of the solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used by QARD to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte true values are unknown to the analyst.

3.12 **Quality Control Sample (QCS)** -- A solution of method analytes of known concentrations that 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 laboratory performance with externally prepared test materials.

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

4.0 INTERFERENCES

4.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.

4.2 The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (7.3 100X) to l00 mL of each standard and sample.

4.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4.4 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

4.5 Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.6 The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

4.7 The quantitation of unretained peaks should be avoided, such as low molecular weight organic acids (formate, acetate, propionate etc.) which are conductive and coelute with or near fluoride and would bias the fluoride quantitation in some drinking and most waste waters.

4.8 Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample purge the sample with an inert gas (argon or nitrogen) for about five minutes or until no chlorine dioxide remains.

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 should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

5.3 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS.

5.3.1 Sulfuric acid (Section 7.4)

6.0 EQUIPMENT AND SUPPLIES

6.1 Balance -- Analytical, capable of accurately weighing to the nearest 0.000l g.

6.2 Ion chromatograph -- Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gasses and detectors.

6.2.1 Anion guard column: A protector of the separator column. If omitted from the system the retention times will be shorter. Usually packed with a substrate the same as that in the separator column.

6.2.2 Anion separator column: This column produces the separation shown in Figures 1 and 2.

6.2.2.1 Anion analytical column (Method A): The separation shown in Figure 1 was generated using a Dionex AS4A column (P/N 37041). An optional column may be used if comparable resolution of peaks is obtained, and the requirements of Section 9.2 can be met.

6.2.2.2 Anion analytical column (Method B): The separation shown in Figure 2 was generated using a Dionex AS9 column (P/N 42025). An optional column may be used if comparable resolution of peaks is obtained and the requirements of Section 9.2 can be met.

6.2.3 Anion suppressor device: The data presented in this method were generated using a Dionex anion micro membrane suppressor (P/N 37106).

6.2.4 Detector -- Conductivity cell: Approximately 1.25 µL internal volume, (Dionex, or equivalent) capable of providing data as required in Section 9.2.

6.3 The Dionex AI-450 Data Chromatography Software was used to generate all the data in the attached tables. Systems using a stripchart recorder and integrator or other computer based data system may achieve approximately the same MDL's but the user should demonstrate this by the procedure outlined in Section 9.2.

7.0 REAGENTS AND STANDARDS

7.1 Sample bottles: Glass or polyethylene of sufficient volume to allow replicate analyses of anions of interest.

7.2 Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.3 Eluent solution (Method A and Method B): Sodium bicarbonate (CASRN 144-55-8) 1.7 mM, sodium carbonate (CASRN 497-19-8) 1.8 mM. Dissolve 0.2856 g sodium bicarbonate ($NaHCO_3$) and 0.3816 g of sodium carbonate (Na_2CO_3) in reagent water (Section 7.2) and dilute to 2 L.

7.4 Regeneration solution (micro membrane suppressor): Sulfuric acid (CASRN-7664-93-9) 0.025N. Dilute 2.8 mL conc. sulfuric acid (H_2SO_4) to 4 L with reagent water.

7.5 Stock standard solutions, l000 mg/L (1 mg/mL): Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials (dried at 105°C for 30 minutes) as listed below.

7.5.1 Bromide (Br^-) 1000 mg/L: Dissolve 1.2876 g sodium bromide (NaBr, CASRN 7647-15-6) in reagent water and dilute to 1 L.

7.5.2 Bromate (BrO_3^-) 1000 mg/L: Dissolve 1.1798g of sodium bromate ($NaBrO_3$, CASRN 7789-38-0) in reagent water and dilute to 1 L.

7.5.3 Chlorate ($Cl0_3^-$) 1000 mg/L: Dissolve 1.2753g of sodium chlorate ($NaC10_3$, CASRN 7775-09-9) in reagent water and dilute to 1 L.

7.5.4 Chloride (Cl^-) l000 mg/L: Dissolve 1.6485 g sodium chloride (NaCl, CASRN 7647-l4-5) in reagent water and dilute to 1 L.

7.5.5 Chlorite ($Cl0_2^-$) 1000 mg/L: Dissolve 1.3410g of sodium chlorite ($NaC10_2$, CASRN 7758-19-2) in reagent water and dilute to 1 L.

7.5.6 Fluoride (F^-) 1000 mg/L: Dissolve 2.2100g sodium fluoride (NaF, CASRN 7681-49-4) in reagent water and dilute to 1 L.

7.5.7 Nitrate (NO_3^--N) 1000 mg/L: Dissolve 6.0679 g sodium nitrate ($NaNO_3$, CASRN 7631-99-4) in reagent water and dilute to 1 L.

7.5.8 Nitrite (NO_2^--N) 1000 mg/L: Dissolve 4.9257 g sodium nitrite ($NaNO_2$, CASRN 7632-00-0) in reagent water and dilute to 1 L.

7.5.9 Phosphate ($PO^{=}_{4}$-P) 1000 mg/L: Dissolve 4.3937 g potassium phosphate (KH_2PO_4, CASRN 7778-77-0) in reagent water and dilute to 1 L.

7.5.10 Sulfate ($SO_4^{=}$) 1000 mg/L: Dissolve 1.8141 g potassium sulfate (K_2SO_4, CASRN 7778-80-5) in reagent water and dilute to 1 L.

Note: Stability of standards: Stock standards (7.5) are stable for at least one month when stored at 4°C. Except for the chlorite standard which is only stable for two weeks. Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate should be prepared fresh daily.

7.6 Ethylenediamine preservation solution: Dilute 10 mL of ethylenediamine (99%) (CASRN 107-15-3) to 200 mL with reagent water. Use 1 mL of this dilution to each 1 L of sample taken.

8.0 SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis, if required, and minimize waste disposal.

8.2 Sample preservation and holding times for the anions that can be determined by this method are as follows:

Analyte	Preservation	Holding Time
Bromate	None required	28 days
Bromide	None required	28 days
Chlorate	None required	28 days
Chloride	None required	28 days
Chlorite	Cool to 4°C	immediately
Fluoride	None required	28 days
Nitrate-N	Cool to 4°C	48 hours
Combined (Nitrate/Nitrite)	conc. H_2SO_4 to a pH <2	28 days
Nitrite-N	Cool to 4°C	48 hours
0-Phosphate-P	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days

Note: If the determined value for the combined nitrate/nitrite exceeds 0.5 mg/L as N^-, a resample must be analyzed for the individual concentrations of nitrate and nitrite.

8.3 The method of preservation and the holding time for samples analyzed by this method are determined by the anions of interest. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment. It is recommended that all samples

be cooled to 4°C and held for no longer than 28 days for Method A and analyzed immediately in Method B.

Note: If the sample cannot be analyzed for chlorite within ≤10 minutes, the sample may be preserved by adding 1 mL of the ethylenediamine (EDA) preservation solution (Section 7.6) to 1 L of sample. This will preserve the concentration of the chlorite for up to 14 days. This addition of EDA has no effect on bromate or chlorate, so they can also be determined in a sample preserved with EDA. Residual chlorine dioxide should be removed from the sample (per Section 4.8) prior to the addition of EDA.

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 that are generated.

9.2 INITIAL DEMONSTRATION OF PERFORMANCE

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of LCRs and analysis of QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

9.2.2 Linear Calibration Range (LCR) -- The LCR must be determined initially and verified every six months or whenever a significant change in instrument response is observed or expected. The initial demonstration of linearity must use sufficient standards to insure that the resulting curve is linear. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by ±10%, linearity must be reestablished. If any portion of the range is shown to be nonlinear, sufficient standards must be used to clearly define the nonlinear portion.

9.2.3 Quality Control Sample (QCS) -- When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS. If the determined concentrations are not within ±10% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

9.2.4 Method Detection Limit (MDL) -- MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of two

to three times the estimated instrument detection limit.[6] 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 = Student's 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

MDLs should be determined every six months, when a new operator begins work or whenever there is a significant change in the background or instrument response.

9.3 ASSESSING LABORATORY PERFORMANCE

9.3.1 Laboratory Reagent Blank (LRB) -- The laboratory must analyze at least one LRB with each batch of samples. Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.

9.3.2 Laboratory Fortified Blank (LFB) -- The laboratory must analyze at least one LFB with each batch of samples. Calculate accuracy as percent recovery (Section 9.4.2). If the recovery of any analyte falls outside the required control limits of 90-110%, 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 90-110%. When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the percent mean recovery (x) and the standard deviation (S) of the mean 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 90-110%. 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 Solution (IPC) -- For all determinations the laboratory must analyze the IPC (a mid-range check standard) and a calibration blank immediately following daily calibration, after every tenth sample (or more frequently, if required) and at the end of the sample run. Analysis of the IPC solution and calibration blank immediately following calibration must verify that the instrument is within ±10% of calibration. Subsequent analyses of the IPC solution must verify the calibration is still within ±10%. If the calibration cannot be verified within the specified limits, reanalyze the IPC solution. If the second analysis of the IPC solution confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift, 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.

9.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY

9.4.1 Laboratory Fortified Sample Matrix (LFM) -- The laboratory must add a known amount of 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. The analyte concentration must be high enough to be detected above the original sample and should not be less than four times the MDL. The added analyte concentration should be the same as that used in the laboratory fortified blank.

9.4.1.1 If the concentration of fortification is less than 25% of the background concentration of the matrix the matrix recovery should not be calculated.

9.4.2 Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample, and compare these values to the designated LFM recovery range 90-110%. Percent recovery may be calculated using the following equation:

$$R = \frac{C_s - C}{s} x100$$

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

9.4.3 Until sufficient data becomes available (usually a minimum of 20-30 analysis), assess laboratory performance against recovery limits for Method A of 80-120% and 75-125% for Method B. When sufficient internal performance data becomes available develop control limits from percent mean recovery and the standard deviation of the mean recovery.

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 LFM is judged to be either matrix or solution related, not system related.

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.

9.4.6 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options, such as the use of different columns and/or eluents, to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 9.2.

9.4.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and fortification, must be used. Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant performance evaluation sample studies.

9.4.8 At least quarterly, replicates of LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the on-going control charts to document data quality.

9.4.9 When using Part B, the analyst should be aware of the purity of the reagents used to prepare standards. Allowances must be made when the solid materials are less than 99% pure.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Establish ion chromatographic operating parameters equivalent to those indicated in Tables 1A or 1B.

10.2 For each analyte of interest, prepare calibration standards at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more stock standards (Section 7.5) to a volumetric flask and diluting

to volume with reagent water. If a sample analyte concentration exceeds the calibration range the sample may be diluted to fall within the range. If this is not possible then three new calibration concentrations must be chosen, two of which must bracket the concentration of the sample analyte of interest. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

10.3 Using injections of 0.1-1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded.

10.4 The calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 20 samples. If the response or retention time for any analyte varies from the expected values by more than ±10%, the test must be repeated, using fresh calibration standards. If the results are still more than ±10%, a new calibration curve must be prepared for that analyte.

10.5 Nonlinear response can result when the separator column capacity is exceeded (overloading). The response of the detector to the sample when diluted 1:1, and when not diluted, should be compared. If the calculated responses are the same, samples of this total anionic concentration need not be diluted.

11.0 PROCEDURE

11.1 Tables 1A and 1B summarize the recommended operating conditions for the ion chromatograph. Included in these tables are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Section 9.2 are met.

11.2 Check system calibration daily and, if required, recalibrate as described in Section 10.0.

11.3 Load and inject a fixed amount of well mixed sample. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

11.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

11.6 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

Note: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases this peak migration may produce poor resolution or identification.

11.7 The following extraction should be used for solid materials. Add an amount of reagent water equal to 10 times the weight of dry solid material taken as a sample. This slurry is mixed for 10 minutes using a magnetic stirring device. Filter the resulting slurry before injecting using a 0.45 µ membrane type filter. This can be the type that attaches directly to the end of the syringe. Care should be taken to show that good recovery and identification of peaks is obtained with the user's matrix through the use of fortified samples.

11.8 It has been reported that lower detection limits for bromate (≈7 µg/L) can be obtained using a borate based eluent[7]. The use of this eluent or other eluents that improve method performance may be considered as a minor modification of the method and as such still are acceptable.

11.9 Should more complete resolution be needed between peaks the eluent (7.3) can be diluted. This will spread out the run but will also cause the later eluting anions to be retained longer. The analyst must determine to what extent the eluent is diluted. This dilution should not be considered a deviation from the method.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Prepare a calibration curve for each analyte by plotting instrument response against standard concentration. Compute sample concentration by comparing sample response with the standard curve. Multiply answer by appropriate dilution factor.

12.2 Report only those values that fall between the lowest and the highest calibration standards. Samples exceeding the highest standard should be diluted and reanalyzed.

12.3 Report results in mg/L.

12.4 Report NO_2^- as N
NO_3^- as N
HPO_4 as P

13.0 METHODS PERFORMANCE

13.1 Tables 1A and 2A give the single laboratory (EMSL-Cincinnati) MDL for each anion included in the method under the conditions listed.

13.2 Tables 2A and 2B give the single laboratory (EMSL-Cincinnati) standard deviation for each anion included in the method in a variety of waters for the listed conditions.

13.3 Multiple laboratory accuracy and bias data (S_t) and estimated single operator values (S_o) for reagent, drinking and waste water using Method A are given for each anion in Tables 3 through 9. Data from 19 laboratories were used for this data.

13.4 Some of the bias statements, for example chloride and sulfate, may be misleading due to spiking small increments of the anion into large naturally occurring concentrations of the same anion.

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. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 Quantity of the chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 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 Regulations 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. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. 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 waste discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 14.3.

16.0 REFERENCES

1. "Determination of Inorganic Disinfection By-Products by Ion Chromatography", J. Pfaff, C. Brockhoff. J. Am. Water Works Assoc., Vol 82, No. 4, pg 192.

2. Standard Methods for the Examination of Water and Wastewater, Method 4110B, "Anions by Ion Chromatography", 18th Edition of Standard Methods (1992).

3. Dionex, System 4000 Operation and Maintenance Manual, Dionex Corp., Sunnyvale, California 94086, 1988.

4. Method Detection Limit (MDL) as described in "Trace Analyses for Wastewater", J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, Environmental Science and Technology, Vol. 15, Number 12, page 1426, December, 1981.

5. American Society for Testing and Materials. Test Method for Anions in Water by Chemically-Suppressed Ion Chromatography D4327-91. Annual Book of Standards, Vol 11.01 (1993).

6. Code of Federal Regulations 40, Ch. 1, Pt. 136, Appendix B.

7. Hautman, D.P. & Bolyard, M. Analysis of Oxyhalide Disinfection By-products and other Anions of Interest in Drinking Water by Ion Chromatography. Jour. of Chromatog., 602, (1992), 65-74.

17.0 TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 1A. CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS IN REAGENT WATER (PART A)

Analyte	Peak #*	Retention Time (min)	MDL (mg/L)
Fluoride	1	1.2	0.01
Chloride	2	1.7	0.02
Nitrite-N	3	2.0	0.004
Bromide	4	2.9	0.01
Nitrate-N	5	3.2	0.002
o-Phosphate-P	6	5.4	0.003
Sulfate	7	6.9	0.02

Standard Conditions:

Columns: as specified in Sesction 6.2.2.1
Detector: as specified in Section 6.2.4 Pump Rate: 2.0 mL/min.
Eluent: as specified in Section 7.3 Sample Loop: 50 µL

MDL calculated from data system using a y-axis selection of 1000 ns and with a stripchart recorder with an attenuator setting of 1 uMHO full scale.
*See Figure 1

TABLE 1B. CHROMATOGRAPHIC CONDITIONS AND DETECTION LIMITS IN REAGENT WATER (PART B)

Analyte	Peak #*	Retention Time (min)	MDL (mg/L)
Chlorite	1	2.8	0.01
Bromate	2	3.2	0.02
Chlorate	4	7.1	0.003

Standard Conditions:

Column: as specified in Section 6.2.2.2
Detector: as specified in Section 6.2.4 Pump Rate: 1.0 mL/min.
Eluent: as specified in Section 7.3 Sample Loop: 50 µL
Attentuation - 1
y-axis - 500 ns

*See Figure 2

TABLE 2A. SINGLE-OPERATOR ACCURACY AND BIAS OF STANDARD ANIONS (METHOD A)

Analyte	Sample Type	Known Conc. (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)
Bromide	RW	5.0	7	99	0.08
	DW	5.0	7	105	0.10
	SW	5.0	7	95	0.13
	WW	5.0	7	105	0.34
	GW	5.0	7	92	0.34
	SD	2.0	7	82	0.06
Chloride	RW	20.0	7	96	0.35
	DW	20.0	7	108	1.19
	SW	10.0	7	86	0.33
	WW	20.0	7	101	5.2
	GW	20.0	7	114	1.3
	SD	20.0	7	90	0.32
Fluoride	RW	2.0	7	91	0.05
	DW	1.0	7	92	0.06
	SW	1.0	7	73	0.05
	WW	1.0	7	87	0.07
	GW	0.4	7	95	0.07
	SD	5.0	7	101	0.35
Nitrate-N	RW	10.0	7	103	0.21
	DW	10.0	7	104	0.27
	SW	10.0	7	93	0.17
	WW	10.0	7	101	0.82
	GW	10.0	7	97	0.47
	SD	10.0	7	82	0.28
Nitrite	RW	10.0	7	97	0.14
	DW	10.0	7	121	0.25
	SW	5.0	7	92	0.14
	WW	5.0	7	91	0.50
	GW	10.0	7	96	0.35
	SD	2.0	7	98	0.08
o-Phosphate-P	RW	10.0	7	99	0.17
	DW	10.0	7	99	0.26
	SW	10.0	7	98	0.22
	WW	10.0	7	106	0.85
	GW	10.0	7	95	0.33
Sulfate	RW	20.0	7	99	0.40
	DW	50.0	7	105	3.35
	SW	40.0	7	95	1.7
	WW	40.0	7	102	6.4
	GW	40.0	7	112	3.2

TABLE 2A. SINGLE-OPERATOR ACCURACY AND BIAS OF STANDARD ANIONS (METHOD A)

Analyte	Sample Type	Known Conc. (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)

RW = Reagent Water
WW = Mixed Domestic and Industrial Wastewater
DW = Drinking Water
GW = Groundwater
SW = Surface Water
SD = USEPA QC Solid (shale)

TABLE 2B. SINGLE-OPERATOR ACCURACY AND BIAS OF BY-PRODUCT (PART B)

Analyte	Sample Type	Spike (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)
Bromide	RW	5.0	7	103	0.07
		1.0	7	98	0.04
		0.1	7	155	0.005
		0.05	7	122	0.01
	DW	5.0	7	95	0.04
		1.0	7	85	0.02
		0.1	7	98	0.005
		0.05	7	98	0.005
Chlorate	RW	5.0	7	101	0.06
		1.0	7	97	0.01
		0.1	7	100	0.01
		0.05	7	119	0.05
	DW	5.0	7	101	0.04
		1.0	7	115	0.01
		0.1	7	121	0.005
		0.05	7	110	0.01
Chlorite	RW	5.0	7	100	0.04
		1.0	7	98	0.01
		0.1	7	86	0.01
		0.05	7	94	0.01
	DW	5.0	7	96	0.03
		1.0	7	100	0.02
		0.1	7	76	0.00
		0.05	7	96	0.01

RW = Reagent Water
DW = Drinking Water

TABLE 3. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR FLUORIDE

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.26	0.25	0.08	0.11	-3.8
	0.34	0.29	0.11		-14.7
	2.12	2.12	0.07	0.12	0.0
	2.55	2.48	0.14		-2.7
	6.79	6.76	0.20	0.19	-0.4
	8.49	8.46	0.30		-0.4
Drinking	0.26	0.24	0.08	0.05	-7.7
	0.34	0.34	0.11		0.0
	2.12	2.09	0.18	0.06	-1.4
	2.55	2.55	0.16		0.0
	6.79	6.84	0.54	0.25	+0.7
	8.49	8.37	0.75		-1.4
Waste	0.26	0.25	0.15	0.06	-3.8
	0.34	0.32	0.08		-5.9
	2.12	2.13	0.22	0.15	+0.5
	2.55	2.48	0.16		-2.7
	6.79	6.65	0.41	0.20	-2.1
	8.49	8.27	0.36		-2.6

TABLE 4. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR CHLORIDE

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.78	0.79	0.17	0.29	+1.3
	1.04	1.12	0.46		+7.7
	6.50	6.31	0.27	0.14	-2.9
	7.80	7.76	0.39		-0.5
	20.8	20.7	0.54	0.62	-0.5
	26.0	25.9	0.58		-0.4
Drinking	0.78	0.54	0.35	0.20	-30.8
	1.04	0.51	0.38		-51.0
	6.50	5.24	1.35	1.48	-19.4
	7.80	6.02	1.90		-22.8
	20.8	20.0	2.26	1.14	-3.8
	26.0	24.0	2.65		-7.7
Waste	0.78	0.43	0.32	0.39	-44.9
	1.04	0.65	0.48		-37.5
	6.50	4.59	1.82	0.83	-29.4
	7.80	5.45	2.02		-30.1
	20.8	18.3	2.41	1.57	-11.8
	26.0	23.0	2.50		-11.5

TABLE 5. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR NITRITE-NITROGEN

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.36	0.37	0.04	0.04	+2.8
	0.48	0.48	0.06		0.0
	3.00	3.18	0.12	0.06	+6.0
	3.60	3.83	0.12		+6.4
	9.60	9.84	0.36	0.26	+2.5
	12.0	12.1	0.27		+0.6
Drinking	0.36	0.30	0.13	0.03	-16.7
	0.48	0.40	0.14		-16.7
	3.00	3.02	0.23	0.12	+0.7
	3.60	3.62	0.22		+0.6
	9.60	9.59	0.44	0.28	-0.1
	12.0	11.6	0.59		-3.1
Waste	0.36	0.34	0.06	0.04	-5.6
	0.48	0.46	0.07		-4.2
	3.00	3.18	0.13	0.10	+6.0
	3.60	3.76	0.18		+4.4
	9.60	9.74	0.49	0.26	+1.5
	12.0	12.0	0.56		+0.3

TABLE 6. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR BROMIDE

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.63	0.69	0.11	0.05	+9.5
	0.84	0.85	0.12		+1.2
	5.24	5.21	0.22	0.21	-0.6
	6.29	6.17	0.35		-1.9
	16.8	17.1	0.70	0.36	+1.6
	21.0	21.3	0.93		+1.5
Drinking	0.63	0.63	0.13	0.04	0.0
	0.84	0.81	0.13		-3.6
	5.24	5.11	0.23	0.13	-2.5
	6.29	6.18	0.30		-1.7
	16.8	17.0	0.55	0.57	+0.9
	21.0	20.9	0.65		-0.4
Waste	0.63	0.63	0.15	0.09	0.0
	0.84	0.85	0.15		+1.2
	5.24	5.23	0.36	0.11	-0.2
	6.29	6.27	0.46		-0.3
	16.8	16.6	0.69	0.43	-1.0
	21.0	21.1	0.63		+0.3

TABLE 7. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR NITRATE-NITROGEN

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.42	0.42	0.04	0.02	0.0
	0.56	0.56	0.06		0.0
	3.51	3.34	0.15	0.08	-4.8
	4.21	4.05	0.28		-3.8
	11.2	11.1	0.47	0.34	-1.1
	14.0	14.4	0.61		+2.6
Drinking	0.42	0.46	0.08	0.03	+9.5
	0.56	0.58	0.09		+3.6
	3.51	3.45	0.27	0.10	-1.7
	4.21	4.21	0.38		0.0
	11.2	11.5	0.50	0.48	+2.3
	14.0	14.2	0.70		+1.6
Waste	0.42	0.36	0.07	0.06	-14.6
	0.56	0.40	0.16		-28.6
	3.51	3.19	0.31	0.07	-9.1
	4.21	3.84	0.28		-8.8
	11.2	10.9	0.35	0.51	-3.0
	14.0	14.1	0.74		+0.4

TABLE 8. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR ORTHO-PHOSPHATE

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	0.69	0.69	0.06	0.06	0.0
	0.92	0.98	0.15		+6.5
	5.77	5.72	0.36	0.18	-0.9
	6.92	6.78	0.42		-2.0
	18.4	18.8	1.04	0.63	+2.1
	23.1	23.2	0.35		+2.4
Drinking	0.69	0.70	0.17	0.17	+1.4
	0.92	0.96	0.20		+4.3
	5.77	5.43	0.52	0.40	-5.9
	6.92	6.29	0.72		-9.1
	18.4	18.0	0.68	0.59	-2.2
	23.1	22.6	1.07		-2.0
Waste	0.69	0.64	0.26	0.09	-7.2
	0.92	0.82	0.28		-10.9
	5.77	5.18	0.66	0.34	-10.2
	6.92	6.24	0.74		-9.8
	18.4	17.6	2.08	1.27	-4.1
	23.1	22.4	0.87		-3.0

TABLE 9. MULTIPLE LABORATORY (n=19) DETERMINATION OF BIAS FOR SULFATE

Water	Amount Added mg/L	Amount Found mg/L	S_t	S_o	Bias %
Reagent	2.85	2.83	0.32	0.52	-0.7
	3.80	3.83	0.92		+0.8
	23.8	24.0	1.67	0.68	+0.8
	28.5	28.5	1.56		-0.1
	76.0	76.8	3.42	2.33	+1.1
	95.0	95.7	3.59		+0.7
Drinking	2.85	1.12	0.37	0.41	-60.7
	3.80	2.26	0.97		-40.3
	23.8	21.8	1.26	0.51	-8.4
	28.5	25.9	2.48		-9.1
	76.0	74.5	4.63	2.70	-2.0
	95.0	92.3	5.19		-2.8
Waste	2.85	1.89	0.37	0.24	-33.7
	3.80	2.10	1.25		-44.7
	23.8	20.3	3.19	0.58	-14.7
	28.5	24.5	3.24		-14.0
	76.0	71.4	5.65	3.39	-6.1
	95.0	90.3	6.80		-5.0

Method A

Peak	Ret. Time	Ion	mg/L
1	1.17	F^-	2
2	1.73	Cl^-	20
3	2.02	NO_2^-	2
4	2.95	Br^-	2
5	3.20	NO_3^-	10
6	5.38	HPO_4^{2-}	2
7	6.92	SO_4^{2-}	60

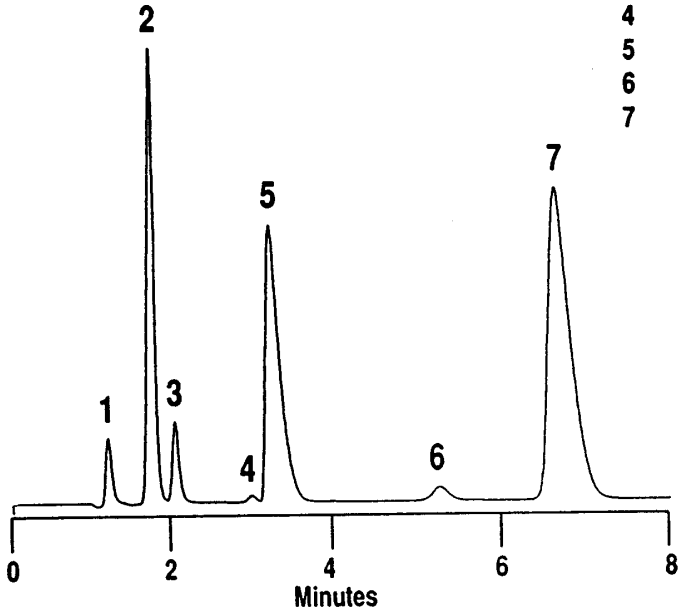

Figure 1. Chromatogram showing separation using the AS4A column

Method B

Peak	Ret. Time	Ion	mg/L
1	2.75	ClO_2^-	0.1
2	3.23	BrO_3^-	0.1
3	3.63	Cl^-	0.1
4	7.08	ClO_3^-	0.1

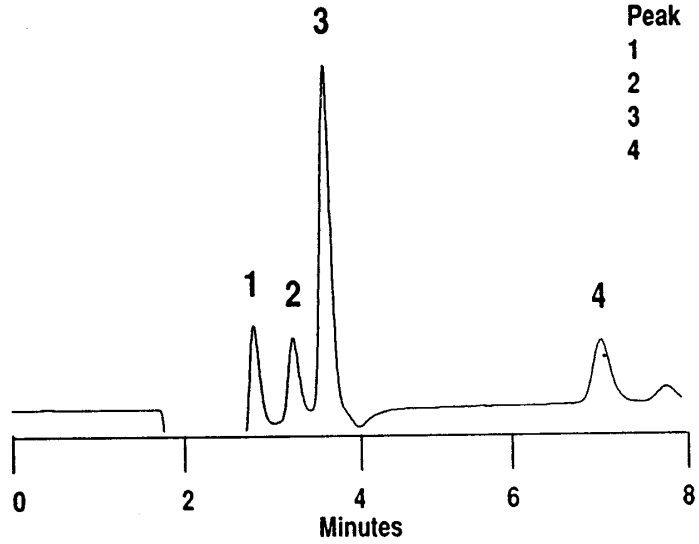

Figure 2. Chromatogram showing separation using the AS9 column

Standard Operating Procedure
Standard Method 2320B
Alkalinity in Drinking Water and Wastewater by Automated Titration

APPROVAL: The undersigned has verified that this SOP is complete and meets requirements specified in document 2D0900100:

Wet Chemistry Manager: _____ Date: 2-5-16

Quality Assurance Director: _____ Date: 2-5-16

1.0 Scope and Application:

1.1 This is an automated titrimetric method applicable to the determination of alkalinity acidity in drinking water and wastewater.

1.2 The specific list of Practical Quantitation Limits (PQL) for each matrix is maintained in the FGL LIMS.

1.3 Prior to the use of this procedure, FGL employees must perform and document an initial demonstration of proficiency for the method and LIMS. For continued use, annual method proficiency must be documented. Refer to 2D0900122 for employee training.

2.0 Summary of Method:

2.1 **Summary:**

2.1.1 The hydroxide, carbonate and bicarbonate are titrated with a known normality of sulfuric acid. The sample is titrated using a pH meter and automated titrator.

2.2 **Definitions:**

2.2.1 Definitions are listed in the FGL Quality Assurance Plan, Section 17.0.

2.3 **Method Modifications:**

2.3.1 This SOP has used a reduction of sample and reagents (in the correct ratios) from the published test method.

3.0 Interferences:

3.1 All glassware must be properly cleaned before use. Refer to 2D0900120 for glassware cleaning.

4.0 Safety:

4.1 A lab coat and gloves should be worn while performing analyses. Protective eyeware must be worn at all times. Refer to the individual MSDS's for safe handling of chemicals.

5.0 Sample Containers, Preservation and Handling:

5.1 Samples should be collected in 1 pint plastic containers.

5.2 Sample preservation is refrigeration at 4° C.

5.3 The holding time is 14 days.
5.4 Procedures for sampling are maintained in the FGL field services department.
5.5 Procedures for sample shipment are maintained in the FGL shipping department.

6.0 Equipment and Supplies:
6.1 Metrohm 855 Robotic Analyzer
6.2 Metrohm 712 Conductemeter
6.3 Computer as specified in SOP 2D0900203

7.0 Quality Control:
7.1 **Preparation Quality Controls:** the batch size for extraction is 20 samples.
7.1.1 Duplicate: One duplicate is analyzed per batch.
7.2 **Analysis Quality Controls:** the batch size for analysis is 20 samples.
7.2.1 pH Initial/Continuing Calibration Verification (ICV/CCV): the ICV is run after the calibration and the CCV is run after every analytical batch and at the end of the analytical run.
7.2.2 Alkalinity Initial/Continuing Calibration Verification (ICV/CCV): the ICV is run at the beginning of the analytical run, after every analytical batch and at the end of the analytical run.
.3 **Detection Limit Quality Controls:**
7.3.1 Method Detection Limit (MDL) determination: For MDL guidance please see SOP 2D0900109.

8.0 Reagent Preparation: N/A
8.1 All reagents received and prepared must be properly labeled and recorded in the LIMS electronic reagent/standard preparation log. Login the reagent using FGL LIMS - Standards. Refer to 2D0900104 for proper reagent preparation and documentation.
8.2 Sufuric Acid Titrant: 0.02N sulfuric acid. Purchase from current vendor.

9.0 Standard Preparation:
9.1 All standards received and prepared must be properly labeled and recorded in the LIMS electronic reagent/standard preparation log. The LIMS then maintains the specific concentrations for each standard mix and subsequent dilutions. Login the standard using FGL LIMS - Standards. Refer to 2D0900104 for proper standard preparation and documentation.
9.2 Record the standard code for all standards on the prep sheet. Also record the volumes of standards used and their concentrations.
9.3 pH Primary Calibration Standard:
9.3.1 Stock: pH 4,pH 7 and pH 10: purchase from current vendor.
9.4 pH Verification Standard:
9.4.1 Stock: pH 8: purchase from current vendor.
9.5 Alkalinity Verification Standard:
9.5.1 Stock: Sodium Carbonate, 99.5% EMD Cat#SX0400-1 or equivalent
9.5.2 Working: 234.9 mg/l sodium carbonate - 0.125 g dried, dessicated Na_2CO_3 in a 500 mL volumetric flask and dilute with deionized water water.
9.6 Titrant
9.6.1 Stock: 0.02 N sulfuric acid. Purchased from current vendor.

10.0 Sample Preparation:

10.1 **LIMS Batching:**

10.1.1 Batch the samples for preparation using FGL LIMS - Preparation. Completely fill in all information requested.

10.1.2 Batch samples for analysis by selecting FGL LIMS -Laboratory.

10.2 **QC Sample Preparation:**

10.2.1 ICV/CCV: to each ICV/CCV cup add 50 mL of standard 9.5.1.

10.2.2 Duplicates: to each of two cups add 50 mL of sample.

10.2.3 Continue the QC samples with step 12.3.

10.3 **Sample Preparation:**

10.3.1 Refer to 2D0900125 for guidance on obtaining a representative sample.

11.0 Calibration:

11.1 **Frequency:**

11.1.1 The pH calibration is performed prior to each analytical run.

11.2 **Procedure and Calculation:**

11.2.1 The system will automatically calibrate the pH probe using the 4, 7 and 10 pH buffers.

11.2.2 The calibration is followed by a calibration verification using a 8.00 pH buffer.

11.3 **Acceptance Criteria:**

11.3.1 The pH verification must be with 95-105%. Do not report pH in LIMS.

11.4 **Failure Resolution:**

11.4.1 If the failure can be corrected by recalibration, then initiate the correction.

11.4.2 If you are unsure of how to handle the failure please contact your supervisor or the QA director.

11.4.3 Refer to 2D0900105 if it is determined that a nonconformance and/or corrective action are required.

12.0 Analytical Procedure:

12.1 **LIMS Batching:** batch the samples for analysis using FGL LIMS - Laboratory

12.2 **Instrument Startup**: Refer to instrument manual for instrument operation.

13.0 Calculations:

13.1 The analysis results are automatically calculated by the instrument.

13.2 Total alkalinity as $CaCO_3$ is calculated as follows:

mL titrant x N acid x 50000 / mL sample

13.3 Samples with a pH of 8.3 or less are calculated as follows:

bicarbonate, (HCO_3) mg/L = mL titrant x N acid x 61000 / mL sample

13.4 Samples with a pH of 8.3 or more are calculated as follows:

13.4.1 If P < 1/2 T:

bicarbonate, (HCO_3) mg/L = [T mL - (2 x P mL)] x N acid x 61000 / mL sample

carbonate, (CO_3) mg/L = 2 x P mL x N acid x 30000 / mL sample

13.4.2 If P = 1/2 T:

carbonate, (CO_3) mg/L = 2 x P mL x N acid x 30000 / mL sample

13.4.3 If P > 1/2 T:

carbonate, (CO_3) mg/L = [2 x (T mL - P mL)] x N acid x 30000 / mL sample

hydroxide, (OH) mg/L = [(2 x P mL) - T mL] x N acid x 17000 / mL sample

13.4.4 If P = T:
hydroxide, (OH) mg/L = Total mL x N acid x 17000 / mL sample

13.5 Conversions

13.5.1 Carbonate Alkalinity as CO_3^{2-} (mg/L) = 0.6 * Carbonate Alkalinity as $CaCO_3$ (mg/L)

13.5.2 Bicarbonate Alkalinity as HCO_3^{2-} (mg/L) = 1.22 * Bicarbonate Alkalinity as $CaCO_3$ (mg/L)

13.5.3 Hydroxide Alkalinity as HCO_3^{2-} (mg/L) = 0.34 * Hydroxide Alkalinity as $CaCO_3$ (mg/L)

14.0 Data Assessment and Failure Resolution:

14.1 All current Data Quality Objectives (DQO's) for quality controls listed below are maintained in the FGL LIMS and automatically checked during data assessment. Qualify the data using FGL LIMS.

14.2 **Preparation Quality Controls:**

14.2.1 Duplicates: the relative percent difference (RPD) of the duplicates should be within the FGL acceptance range based on the control chart.

14.3 **Analysis Quality Controls:**

14.3.1 Alkalinity ICV/CCV: the ICV/CCV must be within the FGL acceptance range of 90-110%.

14.4 **Detection Limit Quality Controls:**

14.4.1 MDL: the MDL must be lower than the PQL.

14.5 **Failure Resolution:**

14.5. If the failure can be corrected by repreparation and/or reanalysis then initiate the correction.

14.5.2 If the failure can't be corrected by repreparation and/or reanalysis or if you are unsure of how to handle the failure please contact your supervisor or the QA director. If the data must be accepted with a failure, an explanation must accompany the failure. Refer to 2D0900113 for guidance on proper handling of failures.

14.5.3 Refer to 2D0900105 if it is determined that a nonconformance and/or corrective action are required.

15.0 Method Performance:

15.1 MDL studies are used to determine precision, accuracy and sensitivity for evaluation of performance at the reporting level. MDL's are electronically stored in the LIMS.

15.2 Control charts are used for analysis and preparation quality controls to determine precision and/or accuracy on an ongoing basis for evaluating the performance of the method. Control charts are electronically maintained in the LIMS. Where applicable the control charts are used to generate the data quality objectives.

15.3 Performance Testing (PT) through interlaboratory studies is performed semi-annually (where applicable) to independently verify performance. PT Study results are maintained in the QA department.

15.4 Refer to the referenced test method(s) for published interlaboratory method performance.

16.0 Review and Reporting:

16.1 **Preparation Review and Reporting:**

16.1.1 Preparation results are reviewed by the analyst. The LIMS batch is set to Pending in LIMS indicating to supervisor or peer that the batch is ready for review. Refer to 2D0900115 for data package review.

16.1.2 Samples are reported in ug/L units. They may be printed on the Prep Summary Report from LIMS; results are stored electronically maintained in the FGL LIMS. Refer to 2D0900112 for data reduction and recording.

16.2 **Analysis Review and Reporting:**

16.2.1 Analysis Data results are reviewed by the analyst. The LIMS batch is set to Pending in LIMS indicating to supervisor or peer that the batch is ready for review. Refer to 2D0900115 for data package review.

16.2.2 Results are electronically maintained in the FGL LIMS. Refer to 2D0900112 for data reduction and recording.

17.0 Record Storage and Archiving:

17.1 **Preparation Records:**

17.1.1 The records generated during preparation are stored electronically in LIMS.

17.1.2 After the Preparation batch has been reviewed, the batch's status is set to Accepted. Refer to 2D0900160 for archiving records.

17.2 **Analysis Records:**

17.2.1 The records generated during analysis are electronically stored in LIMS.

17.2.2 After the Analysis batch has been reviewed, it's Status is set to Accepted. Refer to 2D0900160 for archiving records.

18.0 Maintenance:

18.1 A maintenance log book is utilized to document repair on the instrument. It is imperative that these logs are kept up to date. Log books will be checked for completeness during the annual QA audit. Refer to SOP 2D0900121 for instrument maintenance.

18.2 Specific instrument maintenance information is located in the manufacturers instructions.

18.3 The instrument identification information is maintained in the FGL Quality Assurance Plan.

19.0 Pollution Prevention and Waste Disposal:

19.1 Where feasible, techniques have been used to reduce the amount of standards and reagents in order to minimize the amount of waste generated by this procedure. This is primarily through the proper management of reagents and standards (see sections 8.1 and 9.1) and the reduction of sample and reagents (in the proper ratios) used to perform the procedure.

19.2 Waste from this analysis meets standard sewage discharge requirements. Waste from the analysis may be disposed of down the sink while rinsing with tap water. Samples are kept for one month prior to disposal.

19.3 Any samples found to contain hazardous waste must be given to the Hazardous Waste Officer for proper segregation and disposal.

20.0 References:

20.1 *"Standard Methods for the Examination of Water and Wastewater,"* 20th ed., AWWA, 1998, Method No. 2320B.

21.0 Associated Documents:

21.1 2D0900104 - SOP for Standard/Reagent Preparation and Documentation

21.2 2D0900105 - SOP for Non-conformance/Corrective Action Program

21.3 2D0900109 - SOP for Performing MDL/IDL Studies

21.4 2D0900112 - SOP for Data Reduction and Recording
21.5 2D0900113 - SOP for Qualifying Data
21.6 2D0900115 - SOP for Review of Data Packages by Analysts and Manager
21.7 2D0900120 - SOP for Glassware and Plasticware Cleaning
21.8 2D0900121 - SOP for Instrument Maintenance
21.9 2D0900125 - SOP for Spiking, Diluting and Homogenizing
21.10 2D0900129 - SOP for Analyst Demonstration of Proficiency
21.11 2D0900160 - SOP for Records Archiving, Retrieving and Disposal.
21.12 2D0900200 - SOP for LIMS Raw Data Archiving
21.13 2D0900203 - SOP for PC Workstation Program

Standard Operating Procedure
Standard Method 4500-NO_2 B
Nitrite and Nitrite as N in Drinking Water and Wastewater by UV/VIS Spectrophotometer

APPROVAL: The undersigned has verified that this SOP is complete and meets requirements specified in document 2D0900100:

Wet Chemistry Manager: _____ Date: 2-5-16

Quality Assurance Director: _____ Date: 2/5/16

1.0 Scope and Application:

1.1 This method is based on *"Standard Methods for the Examination of Water and Wastewater,"* AWWA, 20th ed, 2000, Method No. 4500-NO_2 B

1.2 This is a colorimetric method applicable to the determination of Nitrite and Nitrite as N in drinking water and wastewater.

1.3 The specific Practical Quantitation Limits (PQL) for each matrix is maintained in the FGL LIMS.

1.4 Prior to the use of this procedure FGL employees must perform and document an initial demonstration of proficiency for the method and LIMS. For continued use, annual method proficiency must be documented. Refer to 2D0900122 for employee training.

2.0 Summary of Method:

2.1 **Summary:**

2.1.1 Sample is combined with sulfanilamide and N-(1-naphthyl)ethylenediamine dihydrochloride reagents. The resulting compound formed by diazotation of sulfanilamide by nitrite complexes with the naphthyl compound to produce a reddish-purple color.

2.1.2 The concentration is quantified using a five point standard curve prepared using a spectrophotometer set at 543 nm.

2.2 **Definitions:**

2.2.1 Definitions are listed in the FGL Quality Assurance Plan, Section 17.0.

2.3 **Method Modifications:**

2.3.1 This SOP has used a reduction of sample and reagents (in the correct ratios) from the published test method.

3.0 Interferences:

3.1 All glassware must be properly cleaned before use. Refer to 2D0900120 for glassware cleaning.

3.2 The sample cannot be analyzed for nitrite if preserved with sulfuric acid.

3.3 Presence of strong oxidants or reductants in the sample will readily affect the nitrite concentration.
3.4 Suspended solids should be filtered prior to analysis.

4.0 Safety:
4.1 A lab coat and gloves should be worn while performing analyses. Protective eyewear must be worn at all times. Refer to the individual MSDS's for safe handling of chemicals.

5.0 Sample Containers, Preservation and Handling:
5.1 Samples should be collected in 1 pint plastic containers.
5.2 Sample preservation is refrigeration at 4° C.
5.3 The holding time is 48 hrs.
5.4 Procedures for sampling are maintained in the FGL field services department.
5.5 Procedures for sample shipment are maintained in the FGL shipping department.

6.0 Equipment and Materials:
6.1 Perkin Elmer Lambda 35 Spectrophotometer or equivalent spectrophotometer
6.2 8 oz plastic cups

7.0 Quality Control:
7.1 **Preparation Quality Controls:** the batch size for extraction is 20 samples.
7.1.1 Method Blank: one method blank is run per batch.
7.1.2 Matrix Spike (MS): a set of duplicate MS's are run per batch.
7.2 **Analysis Quality Controls:** the batch size for analysis is 10 samples.
7.2.1 Initial/Continuing Calibration Blank (ICB/CCB): the ICB is run after the calibration and the CCB is run after every analytical batch and at the end of the analytical run.
7.2.2 Initial/Continuing Calibration Verification (ICV/CCV): the ICV is run after the calibration and the CCV is run after every analytical batch and at the end of the analytical run.
7.3 **Detection Limit Quality Controls:**
7.3.1 Method Detection Limit (MDL) determination: see SOP 2D0900109.

8.0 Reagent Preparation:
8.1 All reagents received and prepared must be properly labeled and recorded in the LIMS electronic reagent/standard preparation log. Login the reagent using FGL LIMS, Laboratory, Wet Chem, Standards. In order to minimize reagent waste, an appropriate quantity of reagent should be created or purchased which will be completely used during the lifetime of the reagent. Refer to 2D0900104 for proper reagent preparation and documentation.
8.2 Record the reagent code for all reagents on the prep sheet.
8.3 Color reagent: to 400 mL of deionized water add 50 mls of 85% phosphoric acid and 5.0 g sulfanilamide. Stir until dissolved. Add 0.5 g N-(1-naphthyl)ethylenediamine dihydrochloride. Dilute to 500 mL and store in amber bottle. Solution is stable for about 1 month when stored in a dark bottle in a refrigerator.

9.0 Standard Preparation:

9.1 All standards received and prepared must be properly labeled and recorded in the LIMS electronic reagent/standard preparation log.

9.1.1 The LIMS then maintains the specific concentrations for each standard mix and subsequent dilutions.

9.1.2 Login the standard using FGL LIMS-Standards.

9.1.3 In order to minimize standard waste, an appropriate quantity of standard should be created or purchased which will be completely used during the lifetime of the standard.

9.1.4 Refer to 2D0900104 for proper standard preparation and documentation.

9.2 Record the standard code for all standards on the prep references.

9.3 Primary Calibration Standard:

9.3.1 Stock: (1000 mg/L as NO2/ 304.5 mg/L as N): Purchase from current vendor. Store in refrigerator.

9.3.2 Intermediate (4 mg/L as NO2/ 1.2 mg/L as N): dilute 0.4 mL of stock standard in 100 mL deionized water.

9.4 Secondary Calibration Verification Standard: **this standard must be from either a different lot or supplier than the Primary calibration standard.**

9.4.1 Stock: (1000 mg/L as NO2/ 304.5 mg/L as N): order from Ricca as necessary. Store in refrigerator.

9.4.2 Intermediate (3 mg/L as NO2/ 0.46 mg/L as N): dilute 0.3 mL of stock standard (9.4.1) in 200 mL deionized water.

10.0 Sample Preparation:

10.1 **LIMS Batching:**

10.1.1 Batch the samples for preparation using FGL LIMS - Prep.

10.2 **QC Sample Preparation:**

10.2.1 Method Blank: to a 200 mL p-cup add 24 mL of deionized water.

10.2.2 CCV (0.15 mg/L as N): To a 200 mL p-cup, add 2 mL of NO2-N intermediate standard (9.4.2) and 22 mL of deionized water.

10.2.3 MS/MSD: to duplicate 200 mL p-cups add 3 mL aliquots of sample then add 3 mL of intermediate standard (9.3.2) and 18 mL of deionized water.

10.2.4 Continue the QC samples with step 12.2.4.

10.3 **Sample Preparation:**

10.3.1 Refer to 2D0900125 for guidance on obtaining a representative sample.

10.3.2 Samples should be aliquoted using 6 mL of sample and 18 mL of deionized water to 200 mL p-cup.

10.3.3 Turbid samples should be filtered prior to analysis.

11.0 Calibration:

11.1 **Frequency:**

11.1.1 The calibration is performed a minimum of every six months or when continuing calibration verifications indicate a new calibration is required.

11.2 **Procedure and Calculation:**

11.2.1 Calibration standards - dilute following volumes of the intermediate standard (9.3.2) up to 100 mL with deionized water (except 1.2 mg/L level, no dilution)

Levelas N - mg/L	0.012	0.024	0.060	0.24	0.6	1.2
Vol-(9.3.2)	1	2	5	20	50	100

11.2.2 Analyze standards as outlined in section 12.2.
11.2.3 Please refer to section 11.0 of SOP 2D0900020 for the appropriate UV/VIS spectrophotometer calibration.
11.2.4 The calibration calculation is performed by the FGL LIMS.
11.2.5 When finished, put the printout generated in the standard curve logbook and label standards with standard prep codes.

11.3 **Acceptance Criteria:**
11.3.1 The correlation coefficient must be greater that 0.995.

11.4 **Failure Resolution:**
11.4.1 If the failure can be corrected by performing instrument maintenance and/or recalibration then initiate the correction. Log the instrument maintenance performed.
11.4.2 If you are unsure of how to handle the failure please contact your supervisor or the QA director.
11.4.3 Refer to 2D0900105 if it is determined that a nonconformance and/or corrective action are required.

12.0 Analytical Procedure:
12.1 **LIMS Batching:** batch the samples for analysis using FGL LIMS - Analysis.
12.2 **Sample Analysis:**
12.2.1 Set the spectrophotometer wavelength to 543 as outlined in section 12.0 of SOP 2D0900020 for using the spectrophotometer.
12.2.2 Measure 6 mL of each blank, standard, and sample into 100 mL plastic cup.
12.2.3 Add 18 mL of deionized water for a final volume of 24 mL.
12.2.4 Add 1 mL of color reagent every 30 seconds while mixing, and allow 10 minutes for color development.
12.2.5 Rinse the cuvette once with the blank then fill. Place in the instrument cuvette holder making sure that there are no air bubbles or smears present. Autozero the instrument.
12.2.6 Continue in the same manner, using the same cuvette, for check standards, method blanks and samples but do not autozero.
12.2.7 Record the absorbances on the prep sheet, following the procedure outlined in 2D0900020.

13.0 Calculations:
13.1 The absorbances and dilutions are recorded in the Nitrite logbook.
13.2 The aborbacne results are also entered into the LIMS and results calculated by the LIMS.
13.3 The LIMS also converts from NO_2-N to NO_2 if needed.

14.0 Data Assessment and Failure Resolution:

14.1 All current Data Quality Objectives (DQO's) for quality controls listed below are maintained in the FGL LIMS and automatically checked during data assessment. Qualify the data using FGL LIMS..

14.2 **Preparation Quality Controls:**

14.2.1 Method Blank: the method blank must be less than the Practical Quantitation Limit used for reporting (PQL).

14.2.2 MS/BS: the percent recovery and the relative percent difference of the duplicate spikes should be within the FGL acceptance range based on the control chart.

14.3 **Analysis Quality Controls:**

14.3.1 ICB/CCB: the ICB/CCB must be less than the instrument reporting limit (IRL).

14.3.2 ICV/CCV: the ICV/CCV must be within the FGL acceptance range based on the control charts.

14.4 **Detection Limit Quality Controls:**

14.4.1 MDL: the MDL must be lower than the PQL.

14.5 **Failure Resolution:**

14.5.1 If the failure can be corrected by repreparation and/or reanalysis then initiate the correction.

14.5.2 If the failure can't be corrected by repreparation and/or reanalysis or if you are unsure of how to handle the failure please contact your supervisor or the QA director. If the data must be accepted with a failure, an explanation must accompany the failure. Refer to 2D0900113for guidance on proper handling of failures.

14.5.3 Refer to 2D0900105 if it is determined that a nonconformance and/or corrective action are required.

15.0 Method Performance:

15.1 MDL studies are used to determine precision, accuracy and sensitivity for evaluation of performance at the reporting level. MDL's are electronically stored in the LIMS.

15.2 Control charts are used for analysis and preparation quality controls to determine precision and/or accuracy on an ongoing basis for evaluating the performance of the method. Control charts are electronically maintained in the LIMS. Where applicable the control charts are used to generate the data quality objectives.

15.3 Performance Testing (PT) through interlaboratory studies is performed semi-annually (where applicable) to independently verify performance. PT Study results are maintained in the QA department.

15.4 Refer to the referenced test method(s) for published interlaboratory method performance.

16.0 Review and Reporting:

16.1 **Analysis Review and Reporting:**

16.1.1 Analysis result are recorded in the Nitrite logbook and entered into LIMS.

16.1.2 Samples are reported in mg/L units. Refer to 2D0900112 for data reduction and recording.

16.1.3 Analysts Qualifies and Accepts results electronically.

16.2 **Preparation Review and Reporting:**

16.2.1 Samples are reported in mg/L units. Refer to 2D0900112 for data reduction and recording.

16.2.2 Analysts Qualifies and Accepts results electronically.

16.2.3 Lab Director or his representative reviews and approves data for reporting.

17.0 Record Storage and Archiving:

17.1 Results are record in the Nitrite logbook.

17.2 When fewer than ten pages remain in the Nitrite logbook, QA is notified and a new logbook is prepared and issued.

17.3 Returned completed logbooks are archived for five years by QA.

17.4 LIMS maintains the electonic records for minimum five years.

18.0 Maintenance:

18.1 A maintenance log book is utilized to document repair on the instrument. It is imperative that these logs are kept up to date. Refer to SOP 2D0900121 for instrument maintenance.

18.2 The instrument identification information is maintained in the FGL Quality Assurance Plan.

19.0 Pollution Prevention and Waste Disposal:

19.1 Where feasible, techniques have been used to reduce the amount of standards and reagents in order to minimize the amount of waste generated by this procedure. This is primarily through the proper management of reagents and standards (see sections 8.1 and 9.1) and the reduction of sample and reagents (in the proper ratios) used to perform the procedure.

19.2 Waste from this analysis meets standard sewage discharge requirements. Waste from the analysis may be disposed of down the sink while rinsing with tap water. Samples are kept for two months prior to disposal.

20.0 References:

20.1 *"Standard Methods for the Examination of Water and Wastewater,"* AWWA, 20th ed, Method No. 4500-NO_2 B.

21.0 Associated Documents:

21.1 2D0900104 - SOP for Standard/Reagent Preparation and Documentation
21.2 2D0900105 - SOP for Non-conformance/Corrective Action Program
21.3 2D0900109 - SOP for Performing MDL/IDL Studies
21.4 2D0900112 - SOP for Data Reduction and Recording
21.5 2D0900113 - SOP for Qualifying Data
21.6 2D0900115 - SOP for Review of Data Packages by Analysts and Manager
21.7 2D0900120 - SOP for Glassware and Plasticware Cleaning
21.8 2D0900121 - SOP for Instrument Maintenance
21.9 2D0900125 - SOP for Spiking, Diluting and Homogenizing
21.10 2D0900129 - SOP for Analyst Demonstration of Proficiency
21.11 2D0900160 - SOP for Records Archiving, Retrieving and Disposal.

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METHOD 200.7

TRACE ELEMENTS IN WATER, SOLIDS, AND BIOSOLIDS BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

Revision 5.0

January 2001

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Acknowledgments

Revision 5.0 of Method 200.7 was prepared under the direction of William A. Telliard of the U.S. Environmental Protection Agency's (EPA's) Office of Water (OW), Engineering and Analysis Division (EAD) in collaboration with Ted Martin, of EPA's Office of Research and Development's National Exposure Research Laboratory in Cincinnati, Ohio. The method was prepared under EPA Contract 68-C3-0337 and 68-C-98-139 by DynCorp I&ET with assistance from Quality Works, Inc. and Westover Scientific, Inc.

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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)

Disclaimer

This draft method has been reviewed and approved for publication by the Analytical Methods Staff within the Engineering and Analysis Division of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. EPA plans further validation of this draft method. The method may be revised following validation to reflect results of the study. This method version contains minor editorial changes to the October 2000 version.

EPA welcomes suggestions for improvement of this method. Suggestions and questions concerning this method or its application should be addressed to:

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Note: This method is performance based. The laboratory is permitted to omit any step or modify any procedure provided that all performance requirements in this method are met. The laboratory may not omit any quality control analyses. The terms "shall," "must," and "may not" define procedures required for producing reliable results. The terms "should" and "may" indicate optional steps that may be modified or omitted if the laboratory can demonstrate that the modified method produces results equivalent or superior to results produced by this method.

Method 200.7

Trace Elements in Water, Solids, and Biosolids 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 (References 1-4). For analysis of petroleum products see References 5 and 6. 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]	(Ce)	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

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
Yttrium	(Y)	7440-65-5
Zinc	(Zn)	7440-66-6

[a]Cerium has been included as a method analyte for correction of potential inter-element spectral interference.
[b]This method is not suitable for the determination of silica in solids.

1.2 To confirm approval of this method 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, aqueous 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, biosolids (municipal sewage sludge), and solid samples, a digestion/extraction is required prior to analysis when the elements are not in solution (e.g., soil, sludge, sediment, and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing total suspended solids $\geq$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 and sludge 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 or sludge samples containing concentrations of silver >50 mg/kg should be treated in a similar manner.

NOTE: *When analyzing samples containing high levels of silver as might occur in the photographic manufacturing industries, EPA Method 272.1 can be used for silver determinations. Based on the use of cyanogen iodide (CNI) as a stabilizing agent, Method 272.1 can be used on samples containing up to 4 mg/L of Ag. However, it should be recognized that CNI is an extremely hazardous and environmentally toxic reagent, and should be used with the utmost caution.*

1.8 The extraction of tin from solid or sludge samples should be prepared using aliquots <1 g when determined sample concentrations exceed 1%.

1.9 The total recoverable sample digestion procedures 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.

1.10 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.

1.11 This method will be validated in biosolids for those analytes regulated under 40 CFR Part 503 only. It is believed to be applicable for the analysis of biosolids for all analytes listed in Section 1.1. There may be difficulties in analyzing molybdenum in biosolids with a radial ICP, thus the determination of some analytes in biosolids may require the use of an axial ICP. More information will be provided by the validation study.

1.12 Detection limits and linear ranges for the elements will vary with the wavelength selected, the spectrometer, and the matrices. Method detection limits (MDLs; 40 CFR 136, appendix B) and minimum levels (MLs) when no interferences are present will be determined for this method through a validation study. Preliminary MDL values are given in Table 4. The ML for each analyte can be calculated by multiplying the MDL by 3.18 and rounding to the nearest (2, 5, or 10×10^n) where n is an integer.

1.13 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 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 solubilized by gentle refluxing with HNO_3 and HCl. For the total recoverable analysis of a sludge sample containing <1% total suspended solids, analytes are solubilized by successive refluxing with HNO_3 and HCl. For total recoverable analysis of a sludge sample containing total suspended solids $\geq$1% (w/v), analytes are solubilized by refluxing with HNO_3, background organic materials are oxidized with peroxide, and analytes are further solubilized by refluxing with HCl. After cooling, the sample is made up to volume, mixed and then 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 addition of the appropriate volume of HNO_3, and then diluted to a predetermined volume and mixed before analysis.

2.2 The analysis described in this method involves multi-elemental 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 aerosols are 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. The background must be measured adjacent to an analyte wavelength during analysis. Interferences must be considered and addressed appropriately as discussed in Sections 4.0, 7.0, 9.0, and 11.0.

3.0 Definitions

3.1 Biosolids–A solid, semisolid, or liquid residue (sludge) generated during treatment of domestic sewage in a treatment works.

3.2 Calibration blank–A volume of reagent water acidified with the same acid matrix as the calibration standards (Section 7.12.1). The calibration blank is a zero standard and is used to calibrate the ICP instrument.

3.3 Calibration standard–A solution prepared from the dilution of stock standard solutions (Section 7.11). The calibration solutions are used to calibrate the instrument response with respect to analyte concentration.

3.4 Calibration verification (CV) solution–A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria (Section 7.13).

3.5 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 8.2).

3.6 Field blank–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 (Section 8.5). The field blank is analyzed to determine if method analytes or other interferences are present in the field environment.

3.7 Internal standard–Pure analyte(s) added to a sample, extract, or standard solution in a 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 11.6).

3.8 Linear dynamic range (LDR)–The concentration range over which the instrument response to an analyte is linear (Section 9.2.3).

3.9 Matrix spike (MS) and matrix spike duplicate (MSD)–Two aliquots of the same environmental sample to which known quantities of the method analytes are added in the laboratory. The MS and MSD are analyzed exactly like a sample, and their purpose is: to determine whether the sample matrix contributes bias to the analytical results, and to indicate precision associated with laboratory procedures. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations (Section 9.5).

3.10 May–This action, activity, or procedural step is neither required nor prohibited.

3.11 May not–This action, activity, or procedural step is prohibited.

3.12 Method blank–An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are used with other samples. The method blank is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus (Section 7.12.2).

3.13 Method detection limit (MDL)–The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence (Section 9.2.1). The MDL is determined according to procedures described in 40 CFR Part 136, Appendix B.

3.14 Minimum level (ML)–The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specific sample weights, volumes and cleanup procedures have been employed.

3.15 Must–This action, activity, or procedural step is required.

3.16 Ongoing precision and recovery standard (OPR)–The OPR test is used to ensure that the laboratory meets performance criteria during the period that samples are analyzed. It also separates laboratory performance from method performance on the sample matrix. For aqueous samples, the OPR solution is an aliquot of method blank to which known quantities of the method analytes are added in the laboratory. For solid samples, the use of clean sand, soil or peat moss to which known quantities of the method analytes are added in the laboratory is recommended. The OPR is analyzed in the same manner as samples (Section 9.7).

3.17 Plasma solution–A solution that is used to determine the optimum height above the work coil for viewing the plasma (Section 7.16).

3.18 Reference sample–A solution of method analytes of known concentrations which is used to fortify an aliquot of method blank or sample matrix (Section 7.14). The reference sample is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory and/or instrument performance.

3.19 Shall–This action, activity or procedural step is required.

3.20 Should–This action, activity, or procedural step is suggested but not required.

3.21 Solid sample–For the purpose of this method, a sample taken from material classified as either soil, sediment or industrial sludge.

3.22 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 inter-element spectral interferences with respect to a defined set of method criteria (Sections 7.15 and 9.4).

3.23 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 9.5.3.1 and 11.6).

3.24 Standard stock 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 7.10).

3.25 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 sludge, solid, or unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method (Sections 11.2 through 11.4).

3.26 Total Solids–The residue left in the vessel after evaporation of liquid from a sample and subsequent drying in an oven at 103°C to 105°C.

3.27 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 (inter-element 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 inter-element 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 (Reference 8). Users may apply inter-element 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 inter-element corrections are applied, there is a need to verify their accuracy by analyzing spectral interference check solutions as described in Section 7.15. Inter-element 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. Inter-element 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. Inter-element 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 (References 7 and 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 use 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 either be free of off-line inter-element spectral interference or a computer routine must be used for 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 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 9.4 for required spectral interference test criteria.

4.1.5 When inter-element corrections are *not* used, either ongoing SIC solutions (Section 7.15) must be analyzed to verify the absence of inter-element 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 MDL, 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 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 7.12.1). 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 analyzed again after a long rinse period.

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has 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 (References 9, 10, 11, and 12). A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Specifically, concentrated HNO_3 and HCl 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 and digestion 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

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

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 other nonmetallic material.

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

6.10 Labware–Prevention of contamination and loss are of prime consideration for determination of trace levels of elements. 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, and (2) depleting element concentrations through adsorption processes. All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. One recommended procedure found to provide clean labware includes washing with a detergent solution, rinsing with tap water, soaking for four hours or more in 20% (v/v) HNO_3 or a mixture of HNO_3 and HCl (1+2+9), rinsing with reagent water and storing clean (References 2 and 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 Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125-mL to 1-L capacities.

6.10.7 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 should be used whenever possible (Reference 13). 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 (specific gravity = 1.19).

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 (specific gravity = 1.41).

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 (Reference 14).

7.5 Ammonium hydroxide, concentrated (specific gravity = 0.902).

7.6 Tartaric acid–ACS reagent grade.

7.7 Hydrogen peroxide–H_2O_2.

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

7.7.2 Hydrogen peroxide, 30%, stabilized certified reagent grade.

7.8 Clean sand or soil–All references to clean sand or soil in this method refer to sand or soil certified to be free of the analytes of interest at or above their MDLs or to contain those analytes at certified levels.

7.9 Peat moss-All references to peat moss in this method refer to sphagnum peat moss free of arsenic, cadmium, copper, lead, mercury, molybdenum, nickel, selenium and zinc analytes at or above their MDLs (Table 4) or to contain those analytes at certified levels.

7.10 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 (Equations 1 and 2), 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.

Equation 1

From pure element,

$$C = \frac{m}{V}$$

where:

C = concentration (mg/L)
m = mass (mg)
V = volume (L)

Equation 2

From pure compound,

$$C = \frac{(m)(g_f)}{V}$$

where:

C = concentration (mg/L)
m = mass (mg)
V = volume (L)
g_f = gravimetric factor (the weight fraction of the analyte in the compound)

7.10.1 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.

7.10.2 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.

7.10.3 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.

7.10.4 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 de-gas and dissolve compound. Let solution cool and dilute with reagent water in 1-L volumetric flask.

7.10.5 Beryllium solution, stock, 1 mL = 1000 µg Be–DO NOT DRY. Dissolve 19.66 g $BeSO_4 \bullet 4H_2O$ (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.

7.10.6 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 non-glass volumetric flask is recommended to avoid boron contamination from glassware.

7.10.7 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.

7.10.8 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.

7.10.9 Cerium solution, stock, 1 mL = 1000 µg Ce–Make a slurry of 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. Make another slurry of the residue in 20 mL H_2O, add 50 mL concentrated HNO_3, with heat and stirring add 60 mL 50% H_2O_2 drop-wise 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.

7.10.10 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.

7.10.11 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.

7.10.12 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.

7.10.13 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.

7.10.14 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.

7.10.15 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.

7.10.16 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.

7.10.17 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.

7.10.18 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.

7.10.19 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.

7.10.20 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.

7.10.21 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.

7.10.22 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.

7.10.23 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.

7.10.24 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.

7.10.25 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.

7.10.26 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.

7.10.27 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 drop-wise addition of 100 mL (1+1) HCl. Dilute to volume in a 1-L volumetric flask with reagent water.

7.10.28 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.

7.10.29 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.

7.10.30 Titanium solution, stock, 1 mL = 1000 µg Ti–DO NOT DRY. Dissolve 6.138 g $(NH_4)_2TiO(C_2O_4)_2 \bullet H_2O$ (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.

7.10.31 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.

7.10.32 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.

7.10.33 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.

7.11 Mixed calibration standard solutions–For the analysis of total recoverable digested samples, prepare mixed calibration standard solutions 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 that the mixed-standard solutions be transferred to acid-cleaned, never-used FEP fluorocarbon 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.*

7.12 Blanks–Three types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, the method blank is used to assess possible contamination from the sample preparation procedure, and a rinse blank is used to flush the sample uptake system and nebulizer between standards, check solutions, and samples to reduce memory interferences.

7.12.1 The calibration and rinse blanks are prepared by acidifying reagent water to the same concentrations of the acids as used for the standards. The blanks should be stored separately in FEP bottles.

7.12.2 The method blank is reagent water that is carried through the same entire preparation scheme as the samples including sample digestion, when applicable. When the method blank is analyzed, it will contain all the reagents in the same volumes as the samples.

7.13 Calibration verification (CV) solution–The CV solution is used to 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 CV 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 CV solutions be prepared at specified concentrations in order to meet particular program needs.

7.14 Reference sample–Analysis of a reference sample is required for initial and periodic verification of calibration standards or stock standard solutions in order to verify instrument performance. The reference sample 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 reference sample solution should be $\geq$1 mg/L, except silver, which must be limited to a concentration of 0.5 mg/L for solution stability. The reference sample 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. Alternatively, the reference sample may be a standard or certified reference material traceable to the National Institute of Standards and Technology.

7.15 Spectral interference check (SIC) solutions–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) inter-element spectral correction factors for the recommended wavelengths given in Table 1. Other solutions could achieve the same objective as well. Multi-element SIC solutions 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 (Reference 3).

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

7.16 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) HNO_3 and 20 mL (1+1) HCl 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 withdrawing an aliquot 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.

NOTE: *Do not dip pH paper or a pH meter into the sample; remove a small aliquot with a clean pipette and test the aliquot.*

8.2 For the determination of the dissolved elements, a 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 is 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) HNO_3 to pH <2 immediately following filtration.

8.3 For the determination of total recoverable elements in aqueous samples, samples are **not** filtered, but acidified with (1+1) HNO_3 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 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 to 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.

NOTE: *When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood.*

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 A field blank should be prepared and analyzed as required by the data user. Use the same conditions (i.e., container, filtration and preservation) as used in sample collection.

8.6 If a total solids determination is required, then a separate aliquot should be collected following the procedure given in Section 8.0 of Appendix A.

9.0 Quality Assurance/Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 24). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with analyte(s) of interest to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine that results of the analysis meet the performance characteristics of the method.

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

9.1.2 In recognition of advances that are occurring in analytical technology, the analyst is permitted to exercise certain options to eliminate interferences or lower the costs of measurements. These options include alternate digestion, preconcentration, cleanup procedures, and changes in instrumentation. Alternate determinative techniques, such as the substitution of a colorimetric technique or changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in this method is used, then that technique must have a specificity equal to or better than the specificity of the techniques in this method for the analytes of interest.

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

the change will affect calibration, the analyst must recalibrate the instrument according to Section 10.0.

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

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

9.1.2.2.2 A listing of analytes measured, by name and CAS Registry number.

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

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

(a) Method detection limit
(b) Calibration
(c) Calibration verification
(d) Initial precision and recovery
(e) Ongoing precision and recovery
(f) Analysis of blanks
(g) Matrix spike and matrix spike duplicate analyses

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

(a) Sample numbers and other identifiers
(b) Digestion/preparation or extraction dates
(c) Analysis dates and times
(d) Analysis sequence/run chronology
(e) Sample weight or volume
(f) Volume before the extraction/concentration step
(g) Volume after each extraction/concentration step

(h) Final volume before analysis
(i) Injection volume
(j) Dilution data, differentiating between dilution of a sample or extract
(k) Instrument and operating conditions (make, model, revision, modifications)
(l) Sample introduction system (ultrasonic nebulizer, flow injection system, etc.)
(m) Preconcentration system
(n) Operating conditions (background corrections, temperature program, flow rates, etc.)
(o) Detector (type, operating conditions, etc.)
(p) Mass spectra, printer tapes, and other recordings of raw data
(q) Quantitation reports, data system outputs, and other data to link raw data to results reported

9.1.3 Analyses of blanks are required to demonstrate freedom from contamination. Section 9.6 describes the required types, procedures, and criteria for analysis of blanks.

9.1.4 Analyses of MS and MSD samples are required to demonstrate the accuracy and precision of the method and to monitor for matrix interferences (Section 9.5). When results of these spikes indicate atypical method performance for samples, an alternative extraction or cleanup technique must be used to bring method performance within acceptable limits. If method performance cannot be brought within the limits given in this method, the result may not be reported for regulatory compliance purposes.

9.1.5 The laboratory shall, on an ongoing basis, demonstrate through calibration verification (Section 9.3) and through analysis of the OPR standard (Section 9.7) that the analytical system is meeting the performance criteria.

9.1.6 The laboratory shall maintain records to define the quality of data that are generated. Development of accuracy statements is described in Sections 9.5.5.1 and 9.7.7.

9.1.7 All samples must be associated with an acceptable OPR, MS/MSD, IPR, and uncontaminated blanks.

9.2 Initial demonstration of laboratory capability.

9.2.1 Method detection limit–To establish the ability to detect the analyte(s) of interest, the analyst shall determine the MDL for each analyte according to the procedure in 40 CFR 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. The laboratory must produce an MDL that is less than or equal to the MDL specified in Table 4 (to be determined by the validation study) or one-third the regulatory compliance limit, whichever is greater. MDLs must be determined when a new operator begins work or whenever a change in instrument hardware or operating conditions is made that may affect the MDL. MDLs must be determined for solids with clean sand or soil matrix if solid samples are to be run and/or with a reagent water matrix if aqueous samples are to be run. MDLs also must be determined for biosolids with peat moss if sludge samples are to be analyzed for arsenic, cadmium, copper, lead, mercury, molybdenum, nickel, selenium, and zinc.

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

9.2.2.1 Spike four aliquots of reagent water (for aqueous samples) or clean sand or soil (for solid samples) or peat moss (for biosolid samples) with the analyte(s) of interest at one to five times the ML. Analyze the four aliquots according to the procedures in Section 11.0. This test must use the containers, labware, and reagents that will be used with samples and all digestion, extraction, and concentrations steps.

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

9.2.2.3 For each analyte, compare s and X with the corresponding limits for IPR in (Table 5- to be determined in validation study). If s and X for all analyte(s) meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that analyte. Correct the problem and repeat the test.

9.2.3 Linear dynamic range (LDR)–The upper limit of the LDR must be established for each wavelength used. 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 successively higher standard concentrations of the analyte until the observed analyte concentration is no more than 10% below the stated concentration of the standard. 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. Calculated sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and analyzed again. 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 should be redetermined.

9.2.4 Reference sample–When beginning the use of this method, quarterly, and as needed to meet data quality requirements, the analyst must verify the calibration standards and acceptable instrument performance with the preparation and analysis of a reference sample (Section 7.14). To verify the calibration standards, the determined mean concentration from three analyses of the reference sample must be within ±5% of the stated reference sample value. If the reference sample is not within the required limits, an immediate second analysis of the reference sample is recommended to confirm unacceptable performance. If both the calibration standards and acceptable instrument performance cannot be verified, the source of the problem must be identified and corrected before proceeding with further analyses.

9.3 Calibration verification–A laboratory must analyze a CV solution (Section 7.13) and a calibration blank (Section 7.12.1) immediately following daily calibration, after every 10th sample (or more frequently, if required), and at the end of the sample run. The analysis data of the calibration blank and CV solution must be kept on file with the sample analyses data.

9.3.1 The result of the calibration blank should be less than the analyte ML or one-third the regulatory compliance level, whichever is greater.

9.3.2 Analysis of the CV solution immediately following calibration must verify that the instrument is within performance criteria (to be determined by the validation study) (Table 5).

9.3.3 If the calibration cannot be verified within the specified limits, both the CV solution and the calibration blank should be analyzed again. If the second analysis of the CV 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 CV solution must be analyzed again.

9.4 Spectral interference check (SIC) solution–For all determinations the laboratory must periodically verify the inter-element spectral interference correction routine by analyzing SIC solutions (Section 7.15).

9.4.1 For interferences from iron and aluminum, only those correction factors (positive or negative) which, when multiplied by 100, exceed the analyte ML, or one-third the regulatory compliance, whichever is greater, or fall below the lower limit for the calibration blank, need be tested on a daily basis. The lower calibration blank control limit is determined by subtracting the ML, or one-third the regulatory compliance limit, whichever is greater, from zero.

9.4.2 For the other interfering elements, only those correction factors (positive or negative) which, when multiplied by 10 to calculate apparent analyte concentrations that exceed the analyte ML, or one-third the regulatory compliance, whichever is greater, or fall below the lower limit for the calibration blank, need be tested on a daily basis.

9.4.3 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution (Section 7.15, 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 analyte ML, or one-third the regulatory compliance, whichever is greater, 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.*

9.4.4 If the correction factors as 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 inter-element spectral correction factors must be verified annually and updated if necessary.

9.4.5 All inter-element spectral correction factors must be verified whenever there is a change in instrument operating conditions. Examples of changes requiring rigorous verification of spectral correction factors are: changes in incident power, changes in nebulizer gas flow rate, or installation of a new torch injector with a different orifice.

9.4.6 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.

9.4.7 For instruments without inter-element correction capability or when inter-element corrections are not used, SIC solutions (containing similar concentrations of the major components in the samples, e.g., $\geq$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 $\geq$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.

9.5 Matrix spike (MS) and matrix spike duplicates (MSD)-To assess the performance of the method on a given sample matrix, the laboratory must spike, in duplicate, a minimum of 10% (one sample in 10) of the samples from a given sampling site or, if for compliance monitoring, from a given discharge. Blanks may not be used for MS/MSD analysis.

9.5.1 The concentration of the MS and MSD shall be determined as follows:

9.5.1.1 If, as in compliance monitoring, the concentration of analytes in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at 1-5 times the background concentration of the sample, whichever is greater. (For notes on Ag, Sn, and Ba see Sections 1.7, 1.8, and 1.9).

9.5.1.2 If the concentration of analytes in a sample is not being checked against a regulatory concentration limit, the spike shall be at 1-5 times the background concentration.

9.5.1.3 For solid and sludge samples, the concentration added should be expressed as mg/kg and is calculated for a one gram aliquot by multiplying the added analyte concentration in solution (mg/L) by the conversion factor 100 (mg/L x 0.1L/0.001kg = 100, Section 12.5). (For notes on Ag, Sn, and Ba see Sections 1.7, 1.8, and 1.9).

9.5.2 Assessing spike recovery.

9.5.2.1 To determine the background concentration (B), analyze one sample aliquot from each set of 10 samples from each site or discharge according to the procedure in Section 11. If the expected background concentration is known from previous experience or other knowledge, the spiking level may be established *a priori*.

NOTE: *The concentrations of calcium, magnesium, sodium and strontium in environmental waters, along with iron and aluminum in solids and sludge can vary greatly and are not necessarily predictable. Major constituents should not be spiked to >25 mg/L so that the sample matrix is not altered and the analysis is not affected.*

9.5.2.2 Prepare a standard solution to produce an appropriate concentration in the sample (Section 9.5.1).

9.5.2.3 Spike two additional sample aliquots with the spiking solution and analyze these aliquots as described in Section 11 to determine the concentration after spiking (A).

9.5.2.4 Calculate the percent recovery (P) in each aliquot (Equation 3).

Equation 3

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

where:

P = Percent recovery
A = Measured concentration of analyte after spiking
B = Measured concentration of analyte before spiking
T = True concentration of the spike

9.5.3 Compare the percent recovery with the QC acceptance criteria in Table 5 (to be determined in validation study).

9.5.3.1 If P falls outside the designated range for recovery in Table 5, the results have failed to meet the established performance criteria. If P is unacceptable, analyze the OPR standard (Section 9.7). If the OPR is within established performance criteria (Table 5), the analytical system is within specification and the problem can be attributed to interference by the sample matrix. 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 11.6) should be considered.

9.5.3.2 If the results of both the spike and the OPR test fall outside the acceptance criteria, the analytical system is judged to be outside specified limits. The analyst must identify and correct the problem and analyze the sample batch again.

9.5.4 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 11.6.

9.5.4.1 Analyte addition test: An analyte(s) standard added to a portion of a prepared sample, or its dilution, should have a recovery of 85% to 115% of the known value. The analyte(s) addition should produce a minimum level of 20 times and a maximum level of 100 times the method detection limit. If the analyte addition is <20% of the sample analyte concentration, the dilution test described in Section 9.5.4.2 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.

9.5.4.2 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.

9.5.5 Recovery for samples should be assessed and records maintained.

9.5.5.1 After the analysis of five samples of a given matrix type (river water, biosolids, etc.). For which the analyte(s) pass the tests in Section 9.5.3, compute the average percent recovery (P) and the standard deviation of the percent recovery (SP) for the analyte(s). Express the accuracy assessment as a percent recovery interval from P - 2SP to P + 2SP for each matrix. For example, if P = 90% and SP = 10% for five analyses of river water, the accuracy interval is expressed as 70 - 110%.

9.5.5.2 Update the accuracy assessment for each metal in each matrix regularly (e.g., after each five to ten new measurements).

9.5.6 Precision of matrix spike and duplicate.

9.5.6.1 Relative percent difference between duplicates–Compute the relative percent difference (RPD) between the MS and MSD results according to Equation 4 using the concentrations found in the MS and MSD. Do not use the recoveries calculated in Section 9.5.2 for this calculation because the RPD is inflated when the background concentration is near the spike concentration.

Equation 4

$$RPD = 200 * \frac{(|D_1 - D_2|)}{D_1 + D_2}$$

where:

RPD = Relative percent different
D_1 = Concentration of the analyte in the MS sample
D_2 = Concentration of the analyte in the MSD sample

9.5.6.2 The RPD for the MS/MSD pair must not exceed the acceptance criterion in Table 5 (to be determined in validation study). If the criterion is not met, the system is judged to be outside accepted limits of performance. The problem must be identified and corrected, and the analytical batch must be analyzed again.

9.5.6.3 Reference material analysis can provide additional interference 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.

9.6 Blanks.

9.6.1 Method blank.

9.6.1.1 Prepare a method blank with each sample batch (samples of the same matrix - reagent water for aqueous samples, clean sand or soil for solid samples, peat moss for biosolid samples) started through the sample preparation process (Section 11.0) on the same 12-hour shift, to a maximum of 20 samples). Analyze the blank immediately after the OPR is analyzed (Section 9.7) to demonstrate freedom from contamination.

9.6.1.2 If the analyte(s) of interest or any potentially interfering substance is found in the method blank at a concentration equal to or greater than the ML (Table 4, to be determined by the validation study) or 1/3 the regulatory compliance level, whichever is greater, sample analysis must be halted, the source of the contamination determined, the samples must be prepared again with a fresh method blank and OPR and analyzed again.

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

9.6.1.4 If the result for a single blank remains above the ML or if the result for the average concentration plus two standard deviations of three or more blanks exceeds the regulatory compliance level, results for samples associated with those blanks may not be reported for regulatory compliance purposes.

9.6.2 Field blank.

9.6.2.1 Analyze the field blank(s) shipped with each set of samples (samples collected from the same site at the same time, to a maximum of 20 samples). Analyze the blank immediately before analyzing the samples in the batch.

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

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

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

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

9.6.3.1 Bottle blanks–After undergoing appropriate cleaning procedures (Section 6.10), bottles should be subjected to conditions of use to verify the effectiveness of the cleaning procedures. A representative set of sample bottles should be filled with reagent water acidified to pH < 2 and allowed to stand for a minimum of 24 hours. Ideally, the time that the bottles are allowed to stand should be as close as possible to the actual time that sample will be in contact with the bottle. After standing, the water should be analyzed for any signs of contamination. If any bottle shows signs of contamination, the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles cleaned again.

9.6.3.2 Sampler check blanks–Sampler check blanks are generated in the laboratory or at the equipment cleaning contractor's facility by processing reagent water through the sampling devices using the same procedures that are used in the field.

9.6.3.2.1 Sampler check blanks are generated by filling a large carboy or other container with reagent water (Section 7.1) and processing the reagent water through the equipment using the same procedures that are used in the field. For example, manual grab sampler check blanks are collected by directly submerging a sample bottle into the water, filling the bottle, and capping. Subsurface sampler check blanks are collected by immersing the sampler into the water and pumping water into a sample container. Whatever precautions and equipment are used in the field should also be used to generate these blanks.

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

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

9.7 Ongoing precision and recovery.

9.7.1 For aqueous samples, prepare an OPR sample (laboratory fortified method blank) identical to the IPR aliquots (Section 9.2.2.1) with each preparation batch (samples of the same matrix started through the sample preparation process (Section 11.0) on the same 12-hour shift, to a maximum of 20 samples) by spiking an aliquot of reagent water with the analyte(s) of interest.

9.7.2 For solid samples, the use of clean sand or soil fortified as in Section 9.7.1 is recommended.

9.7.3 For biosolid samples, the use of peat moss fortified as in Section 9.7.1 is recommended.

9.7.4 Analyze the OPR sample immediately before the method blank and samples from the same batch.

9.7.5 Compute the percent recovery of each analyte in the OPR sample.

9.7.6 For each analyte, compare the concentration to the limits for ongoing recovery in (Table 5 - to be determined in validation study). If all analyte(s) meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual recovery falls outside of the range given, the analytical processes are not being performed properly for that analyte. Correct the problem, prepare the sample batch again with fresh OPR and method blank, and reanalyze the QA/QC and samples.

9.7.7 Add results that pass the specifications in Section 9.7.6 to IPR and previous OPR data for each analyte in each matrix. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each analyte in each matrix type by calculating the average percent recovery (P) and the standard deviation of percent recovery (SP). Express the accuracy as a recovery interval from P - 2SP to P + 2SP. For example, if P = 95% and SP = 5%, the accuracy is 85 - 105%.

10.0 Calibration and Standardization

10.1 For initial and daily operation, calibrate the instrument according to the instrument manufacturer's recommended procedures, using mixed calibration standard solutions (Section 7.11).

10.2 The calibration line should include at least three non-zero points with the high standard near the upper limit of the linear dynamic range (Section 9.2.3) and the low standard that contains the analyte(s) of interest at the ML (Section 1.12, Table 4, to be determined during the validation study). Replicates of a calibration blank (Section 7.13.1) and the 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 (Reference 20).

10.3 Calculate the slope and intercept of a line using weighted linear regression. Use the inverse of the standard's concentration squared ($1/x^2$) as the weighting factor. The calibration is acceptable if the R^2 is greater than 0.995 and the absolute value of the intercept is less than the MDL for the target analyte. If

these conditions are not met, then the laboratory may not report data analyzed under that calibration and must recalibrate the instrument.

10.4 The concentration of samples is determined using Equation 5.

Equation 5

$$y = mx + b$$

where *y = sample concentration*
m = slope (calculated in Section 10.3)
x = instrument response
b = intercept (calculated in Section 10.3)

10.5 Response factor may be calculated as an alternative to weighted linear regression for instrument calibration. Calculate the response factor (RF) at each concentration, as follows:

Equation 6

$$RF = \frac{R_x}{C_x}$$

where:
R_x = Peak height or area
C_x = Concentration of standard x

10.5.1 Calculate the mean response factor (RF_m), the standard deviation of the RF_m, and the relative standard deviation (RSD) of the mean (Equation 7).

Equation 7

$$RSD = 100 * \frac{SD}{RF_m}$$

where:
RSD = Relative standard deviation of the mean
SD = Standard deviation of the RF_m
RF_m = the mean response factor

10.5.2 Performance criteria for the calibration will be calculated after the validation of the method.

11.0 Procedure

11.1 Aqueous sample preparation (Dissolved analytes)–For the determination of dissolved analytes in ground, drinking and surface waters, pipet an aliquot ($\geq$20 mL) of the filtered, acid preserved sample into a 50-mL polypropylene centrifuge tube. Add an appropriate volume of (1+1) HNO_3 to adjust the acid concentration of the aliquot to approximate a 1% (v/v) HNO_3 solution (e.g., add 0.2 mL (1+1) HNO_3 to a 20 mL aliquot of sample). Cap the tube and mix. The sample is now ready for analysis. Allowance for sample dilution should be made in the calculations (Section 12). 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.

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 while making allowance for sample dilution in the data calculation (Section 12.0). 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 of >1 NTU turbidity, transfer a 100 mL (±1 mL) aliquot from a well mixed, acid preserved sample to a 250-mL Griffin beaker. (When necessary, smaller sample aliquot volumes may be used).

NOTE: *If the sample contains <u>undissolved</u> 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) HNO_3 and 1.0 mL of (1+1) HCl 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, dilute 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 to a tared weighing dish. For samples with <35% estimated moisture, a 20 g portion is sufficient. For samples with estimated moisture >35%, a larger aliquot 50-100 g is required. Dry the sample to a constant weight at 60°C. 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, but 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.

11.3.7 Determine the total solids content of the sample using the procedure in Appendix A.

11.4 Sludge sample preparation–Total recoverable analytes.

NOTE: *It may be possible to use the solids digestion (Section 11.3) for sludge samples, depending on the composition of the sludge sample and the analyte(s) of interest. Under this performance-based method, it is admissible to change the digestion technique as long as all quality control and assurance tests meet the criteria published in Tables 4 and 5. This method has been validated using the sludge sample digestion in Section 11.4 of this method, and it works for all the analytes listed in Section 1.1.*

11.4.1 Determination of total recoverable analytes in sludge samples containing total suspended solids $\geq$1% (w/v).

11.4.1.1 Mix the sample thoroughly and transfer a portion to a tared weighing dish. For samples with <35% estimated moisture a 20 g portion is sufficient. For samples with estimated moisture >35% a larger aliquot of 50-100 g is required. Dry the sample to a constant weight at 60°C. 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.

11.4.1.2 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).

11.4.1.3 Add 10 mL of (1+1) HNO_3 to the beaker and cover the lip of the beaker with a watch glass. Place the beaker on a hot plate and reflux the sample for 10 minutes. Remove the sample from the hot plate and allow to cool. Add 5 mL of concentrated HNO_3 to the beaker, replace the watch glass, place on a hot plate, and reflux for 30 minutes. Repeat this last step once. Remove the beaker from the hot plate and allow the sample to cool. Add 2 mL of reagent water and 3 mL of 30% H_2O_2. Place the beaker on a hot plate and heat the sample until a gentle effervescence is observed. Once the reaction has subsided, additional 1 mL aliquots of the 30% H_2O_2 should be added until no effervescence is observed, but to no more than a total of 10 mL. Add 2 mL concentrated HCl and 10 mL of reagent water to the sample, cover with a watch glass and reflux for 15 minutes.

11.4.1.4 Cool the sample and dilute to 100 mL with reagent water. Any remaining solid material should be allowed to settle, or an aliquot of the final sample volume may be centrifuged.

11.4.1.5 Determine the total solids content of the sample using the procedure in Appendix A.

11.4.2 Determination of total recoverable analytes in sludge samples containing total suspended solids < 1% (w/v).

11.4.2.1 Transfer 100 mL of well-mixed sample to a 250-mL Griffin beaker.

11.4.2.2 Add 3 mL of concentrated HNO_3 and place the beaker on a hot plate. Heat the sample and cautiously evaporate to a volume of 5 mL. If the sample contains large amounts of dissolved solids, adjust this volume upwards to prevent the sample from going to dryness. Remove the beaker from the hot plate and allow the sample to cool. Add 3 mL of concentrated HNO_3, cover with a watch glass and gently reflux the sample until the sample is completely digested or no further changes in appearance occur, adding additional aliquots of acid if necessary to prevent the sample from going to dryness. Then remove the watch glass and reduce the sample volume to 3 mL, again adjusting upwards if necessary.

11.4.2.3 Cool the beaker, then add 10 mL of reagent water and 4 mL of (1+1) HCl to the sample and reflux for 15 minutes. Cool the sample and dilute to 100 mL with reagent water. Any remaining solid material should be allowed to settle, or an aliquot of the final sample volume may be centrifuged.

11.4.2.4 Determine the total solids content of the sample using the procedure in Appendix A.

11.5 Sample analysis.

11.5.1 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.

11.5.2 Configure the instrument system.

11.5.2.1 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 (Reference 17).

11.5.2.2 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.

11.5.2.3 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 7.10.32), 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 (Reference 18). Record the nebulizer gas flow rate or pressure setting for future reference.

11.5.2.4 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.

11.5.2.5 After horizontally aligning the plasma and/or optically profiling the spectrometer, use the selected instrument conditions from Sections 11.5.2.3 and 11.5.2.4, and aspirate the plasma solution (Section 7.16), 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 (Reference 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 for the least sensitive element or accept a compromise position of the intensity ratios of all four analytes.

11.5.2.6 The instrument operating condition finally selected as optimum should provide the lowest reliable method detection limits.

11.5.2.7 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.

11.5.2.8 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 inter-element 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.

11.5.3 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.

11.5.4 Prior to and during the analysis of samples, the laboratory must comply with the required QA/QC procedures (Section 9). QA/QC data must be generated using the same instrument operating conditions (Section 11.5) and calibration routine (Section 10) in effect for sample analysis. The data must be documented and kept on file so that they are available for review by the data user.

11.5.5 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 7.12.1) for a minimum of 60 seconds (Section 4.4) between all standard or sample solutions, OPRs, MS, MSD, and check solutions.

11.5.6 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 analyzed again.

11.5.7 Also, for the inter-element spectral interference correction routines to remain valid during sample analysis, the interferant concentration must not exceed its LDR. If the interferant LDR is exceeded, analyte detection limits are raised and determination by another approved test procedure that is either more sensitive and/or interference free is recommended. If another approved method is unavailable, the sample may be diluted with acidified reagent water and reanalyzed.

11.5.8 When it is necessary to assess an operative matrix interference (e.g., signal reduction due to high dissolved solids), the tests described in Section 9.5.4 and 11.6 are recommended.

11.5.9 Report data as directed in Section 12.0.

11.6 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 compensates

for enhancement or depression of an analyte signal by a matrix (Reference 21). It will not correct for additive interferences such as contamination, inter-element 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 with Equation 8.

Equation 8

$$C_S = \frac{S_2 * V_1 * C}{(S_1 - S_2) * V_2}$$

where:

C_s = *Sample concentration (mg/L)*
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 inter-element 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 and sludge 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 MDL.

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 an 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.

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 hundredth place and report analyte concentrations up to three significant figures. Extract concentrations for solids and sludge data should be rounded in a similar manner before calculations in Section 12.5 are performed.

12.5 For total recoverable analytes in solid and sludge samples (Sections 11.3 and 11.4), 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 Equation 9.

Equation 9

$$C_S = \frac{C * V * D}{W}$$

where:

C_s=Sample concentration (mg/kg, dry-weight basis)
C=Concentration in extract (mg/L)
V=Volume of extract (L, 100 mL = 0.1L)
D=Dilution factor (undiluted = 1)
W=Dry weight of sample aliquot extracted (kg, 1g = 0.001kg)

Do not report analyte data below the solids MDL.

12.6 To report percent solids or mg/kg of solid and sludge samples, use the procedure in Appendix A.

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 MDLs and MLs will be determined in a validation study. Preliminary MDL values are given in Table 4. The ML for each analyte can be calculated by multiplying

the MDL by 3.18 and rounding to the number nearest (2, 5, or 10 X 10^n) where n is a positive or negative integer.

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 7.10). 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 are provided only as a guide to instrumental limits (Reference 16). 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 (Reference 2). Other calibration limits in the linear ranges may be used.

[d]Calculated from 2-sigma data (Reference 5).

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

TABLE 2: ON-LINE METHOD INTER-ELEMENT SPECTRAL INTERFERENCES ARISING FROM INTERFERANTS AT THE 100 mg/L LEVEL

Analyte	Wavelength (nm)	Interferant[a]
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

[a]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
II	Se
III	K, Li, Mo, Na, Sr, and Ti
IV	Co, P, V, and Ce
V	Al, Cr, Hg, SiO_2, Sn, and Zn
	Be, Fe, Mg, Ni, Pb, and Tl

TABLE 4: TOTAL RECOVERABLE METHOD DETECTION LIMITS (MDL)[a]

	MDLs	
Analyte	**Aqueous, mg/L[b]**	**Solids, mg/kg[c]**
Ag	0.002	0.3
Al	0.02	3
As	0.008	2
B[d]	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[e]	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
Y		
Zn	0.002	0.3

[a] Table will be changed after interlaboratory validation of Method 200.7.

[b] 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.

[c] Estimated, calculated from aqueous MDL determinations.

[d] Boron not reported because of glassware contamination. Silica not determined in solid samples.

[e] Elevated value due to fume-hood contamination.

TABLE 5: PERFORMANCE CRITERIA FOR METHOD 200.7 (TO BE DETERMINED DURING INTERLABORATORY VALIDATION)

Pb-Cu ICP-AES EMISSION PROFILE

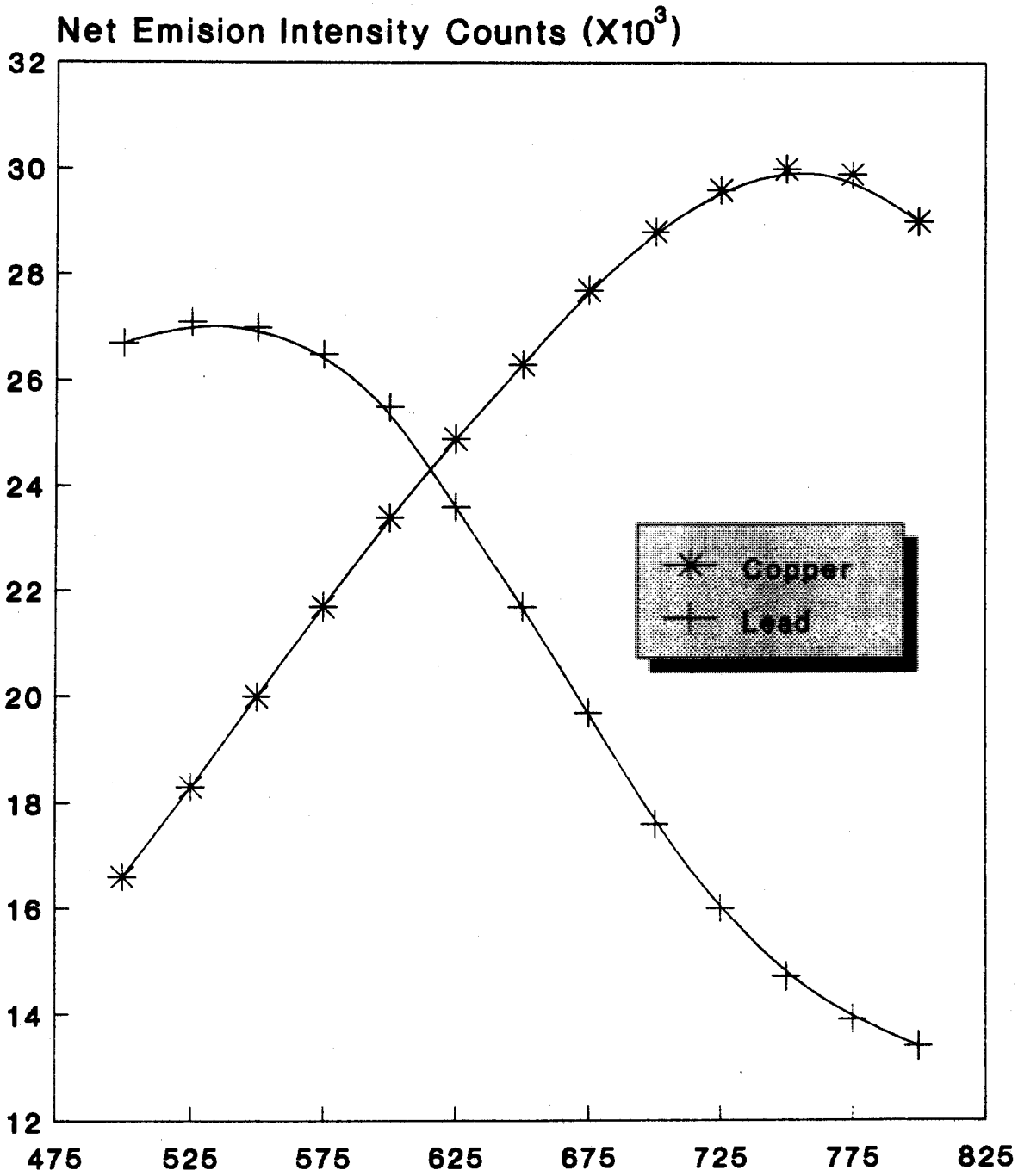

Figure 1

Appendix A: Total Solids in Solid and Semisolid Matrices

1.0 Scope and Application

1.1 This procedure is applicable to the determination of total solids in such solid and semisolid samples as soils, sediments, biosolids (municipal sewage sludge) separated from water and wastewater treatment processes, and sludge cakes from vacuum filtration, centrifugation, or other biosolids dewatering processes.

1.2 This procedure is taken from EPA Method 1684: *Total, Fixed, and Volatile Solids in Solid and Semi-Solid Matrices.*

1.3 Method detection limits (MDLs) and minimum levels (MLs) have not been formally established for this draft procedure. These values will be determined during the validation of Method 1684.

1.4 This procedure is performance based. The laboratory is permitted to omit any step or modify any procedure (e.g. to overcome interferences, to lower the cost of measurement), provided that all performance requirements in this procedure are met. Requirements for establishing equivalency are given in Section 9.1.2 of Method 200.7.

1.5 Each laboratory that uses this procedure must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.

2.0 Summary of Method

2.1 Sample aliquots of 25-50 g are dried at 103°C to 105°C to drive off water in the sample.

2.3 The mass of total solids in the sample is determined by comparing the mass of the sample before and after each drying step.

3.0 Definitions

3.1 Total Solids–The residue left in the vessel after evaporation of liquid from a sample and subsequent drying in an oven at 103°C to 105°C.

3.2 Additional definitions are given in Sections 3.0 of Method 200.7.

4.0 Interferences

4.1 Sampling, subsampling, and pipeting multi-phase samples may introduce serious errors (Reference 13.1). Make and keep such samples homogeneous

during transfer. Use special handling to ensure sample integrity when subsampling. Mix small samples with a magnetic stirrer. If visible suspended solids are present, pipet with wide-bore pipets. If part of a sample adheres to the sample container, intensive homogenization is required to ensure accurate results. When dried, some samples form a crust that prevents evaporation; special handling such as extended drying times are required to deal with this. Avoid using a magnetic stirrer with samples containing magnetic particles.

4.2 The temperature and time of residue drying has an important bearing on results (Reference 1). Problems such as weight losses due to volatilization of organic matter, and evolution of gases from heat-induced chemical decomposition, weight gains due to oxidation, and confounding factors like mechanical occlusion of water and water of crystallization depend on temperature and time of heating. It is therefore essential that samples be dried at a uniform temperature, and for no longer than specified. Each sample requires close attention to desiccation after drying. Minimize the time the desiccator is open because moist air may enter and be absorbed by the samples. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

4.3 Residues dried at 103°C to 105°C may retain some bound water as water of crystallization or as water occluded in the interstices of crystals. They lose CO_2 in the conversion of bicarbonate to carbonate. The residues usually lose only slight amounts of organic matter by volatilization at this temperature. Because removal of occluded water is marginal at this temperature, attainment of constant weight may be very slow.

4.4 Results for residues high in oil or grease may be questionable because of the difficulty of drying to constant weight in a reasonable time.

4.5 The determination of total solids is subject to negative error due to loss of ammonium carbonate and volatile organic matter during the drying step at 103°C to 105°C. Carefully observe specified ignition time and temperature to control losses of volatile inorganic salts if these are a problem.

5.0 Safety

5.1 Refer to Section 5.0 of Method 200.7 for safety precautions.

6.0 Equipment and Supplies

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

6.1 Evaporating Dishes–Dishes of 100-mL capacity. The dishes may be made of porcelain (90-mm diameter), platinum, or high-silica glass.

6.2 Watch glass–Capable of covering the evaporating dishes (Section 6.1).

6.3 Steam bath.

6.4 Desiccator–Moisture concentration in the desiccator should be monitored by an instrumental indicator or with a color-indicator desiccant.

6.5 Drying oven–Thermostatically-controlled, capable of maintaining a uniform temperature of 103°C to 105°C throughout the drying chamber.

6.6 Analytical balance–Capable of weighing to 0.1 mg for samples having a mass up to 200 g.

6.7 Container handling apparatus–Gloves, tongs, or a suitable holder for moving and handling hot containers after drying.

6.8 Bottles–Glass or plastic bottles of a suitable size for sample collection.

6.9 Rubber gloves (Optional).

6.10 No. 7 Cork borer (Optional).

7.0 Reagents and Standards

7.1 Reagent water–Deionized, distilled, or otherwise purified water.

7.2 Sodium chloride-potassium hydrogen phthalate standard (NaCl-KHP).

7.2.1 Dissolve 0.10 g sodium chloride (NaCl) in 500 mL reagent water. Mix to dissolve.

7.2.2 Add 0.10 g potassium hydrogen phthalate (KHP) to the NaCl solution (Section 7.2.1) and mix. If the KHP does not dissolve readily, warm the solution while mixing. Dilute to 1 L with reagent water. Store at 4°C. Assuming 100% volatility of the acid phthalate ion, this solution contains 200 mg/L total solids, 81.0 mg/L volatile solids, and 119 mg/L fixed solids.

8.0 Sample Collection, Preservation, and Storage

8.1 Use resistant-glass or plastic bottles to collect sample for solids analysis, provided that the material in suspension does not adhere to container walls. Sampling should be done in accordance with Reference 13.2. Begin analysis as soon as possible after collection because of the impracticality of preserving the

sample. Refrigerate the sample at 4°C up to the time of analysis to minimize microbiological decomposition of solids. Preferably do not hold samples more than 24 hours. Under no circumstances should the sample be held more than seven days. Bring samples to room temperature before analysis.

9.0 Quality Control

9.1 Quality control requirements and requirements for performance-based methods are given in Section 9.1 of Method 200.7.

9.2 Initial demonstration of laboratory capability - The initial demonstration of laboratory capability is used to characterize laboratory performance and method detection limits.

9.2.1 Method detection limit (MDL) - The method detection limit should be established for the analyte, using diluted NaCl-KHP standard (Section 7.2). To determine MDL values, take seven replicate aliquots of the diluted NaCl-KHP solution and process each aliquot through each step of the analytical method. Perform all calculations and report the concentration values in the appropriate units. MDLs should be determined every year or whenever a modification to the method or analytical system is made that will affect the method detection limit.

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

9.2.2.1 Prepare four samples by diluting NaCl-KHP standard (Section 7.2) to 1-5 times the MDL. Using the procedures in Section 11, analyze these samples for total solids.

9.2.2.2 Using the results of the four analyses, compute the average percent recovery (x) and the standard deviation (s, Equation 1) of the percent recovery for total solids.

Equation 1

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

Where:

n = number of samples
x = % recovery in each sample
s = standard deviation

9.2.2.3 Compare s and x with the corresponding limits for initial precision and recovery in Table 2 (to be determined in validation study). If s and x meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or x falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.3 Laboratory blanks

9.3.1 Prepare and analyze a laboratory blank initially (i.e. with the tests in Section 9.2) and with each analytical batch. The blank must be subjected to the same procedural steps as a sample, and will consist of approximately 25 g of reagent water.

9.3.2 If material is detected in the blank at a concentration greater than the MDL (Section 1.3), analysis of samples must be halted until the source of contamination is eliminated and a new blank shows no evidence of contamination. All samples must be associated with an uncontaminated laboratory blank before the results may be reported for regulatory compliance purposes.

9.4 Ongoing Precision and Recovery

9.4.1 Prepare an ongoing precision and recovery (OPR) solution identical to the IPR solution described in Section 9.2.2.1.

9.4.2 An aliquot of the OPR solution must be analyzed with each sample batch (samples started through the sample preparation process (Section 11) on the same 12-hour shift, to a maximum of 20 samples).

9.4.3 Compute the percent recovery of total solids in the OPR sample.

9.4.4 Compare the results to the limits for ongoing recovery in Table 2 (to be determined in validation study). If the results meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, the recovery of total solids falls outside of the range given, the analytical processes are not being performed properly. Correct the problem, reprepare the sample batch, and repeat the OPR test. All samples must be associated with an OPR analysis that passes acceptance criteria before the sample results can be reported for regulatory compliance purposes.

9.4.5 results that pass the specifications in Section 9.4.4 to IPR and previous OPR data. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory

accuracy for each analyte by calculating the average percent recovery (R) and the standard deviation of percent recovery (SR). Express the accuracy as a recovery interval from R-2SR to R+2SR. For example, if R=05% and SR=5%, the accuracy is 85-115%.

9.5 Duplicate analyses

9.5.1 Ten percent of samples must be analyzed in duplicate. The duplicate analyses must be performed within the same sample batch (samples whose analysis is started within the same 12-hour period, to a maximum of 20 samples).

9.5.2 The total solids of the duplicate samples must be within 10%.

10.0 Calibration and Standardization

10.1 Calibrate the analytical balance at 2 mg and 1000 mg using class "S" weights.

10.2 Calibration shall be within ± 10% (i.e. ±0.2 mg) at 2 mg and ± 0.5% (i.e. ±5 mg) at 1000 mg. If values are not within these limits, recalibrate the balance.

11.0 Procedure

11.1 Preparation of evaporating dishes–Heat dishes and watch glasses at 103°C to 105°C for 1 hour in an oven. Cool and store the dried equipment in a desiccator. Weigh each dish and watch glass prior to use (record combined weight as "W_{dish}").

11.2 Preparation of samples

11.2.1 Fluid samples–If the sample contains enough moisture to flow readily, stir to homogenize, place a 25 to 50 g sample aliquot on the prepared evaporating dish. If the sample is to be analyzed in duplicate, the mass of the two aliquots may not differ by more than 10%. Spread each sample so that it is evenly distributed over the evaporating dish. Evaporate the samples to dryness on a steam bath. Cover each sample with a watch glass, and weigh (record weight as "W_{sample}").

NOTE: *Weigh wet samples quickly because wet samples tend to lose weight by evaporation. Samples should be weighed immediately after aliquots are prepared.*

11.2.2 Solid samples–If the sample consists of discrete pieces of solid material (dewatered sludge, for example), take cores from each piece with a No. 7 cork borer or pulverize the entire sample coarsely on a clean surface by hand, using rubber gloves. Place a 25 to 50 g sample aliquot of the pulverized sample on the prepared evaporating dish. If the sample is to

be analyzed in duplicate, the mass of the two aliquots may not differ by more than 10%. Spread each sample so that it is evenly distributed over the evaporating dish. Cover each sample with a watch glass, and weigh (record weight as "W_{sample}").

11.3 Dry the samples at 103°C to 105°C for a minimum of 12 hours, cool to balance temperature in an individual desiccator containing fresh desiccant, and weigh. Heat the residue again for 1 hour, cool it to balance temperature in a desiccator, and weigh. Repeat this heating, cooling, desiccating, and weighing procedure until the weight change is less than 5% or 50 mg, whichever is less. Record the final weight as "W_{total}."

NOTE: *It is imperative that dried samples weighed quickly since residues often are very hygroscopic and rapidly absorb moisture from the air. Samples must remain in the dessicator until the analyst is ready to weigh them.*

12.0 Data Analysis and Calculations

12.1 Calculate the % solids or the mg solids/kg sludge for total solids (Equation 2).

Equation 2

$$\%\ total\ solids = \frac{W_{total} - W_{dish}}{W_{sample} - W_{dish}} * 100$$

or

$$\frac{mg\ total\ solids}{kg\ sludge} = \frac{W_{total} - W_{dish}}{W_{sample} - W_{dish}} * 1{,}000{,}000$$

Where:

W_{dish}=*Weight of dish (mg)*
W_{sample}=*Weight of wet sample and dish (mg)*
W_{total}=*Weight of dried residue and dish (mg)*

12.2 Sample results should be reported as % solids or mg/kg to three significant figures. Report results below the ML as < the ML, or as required by the permitting authority or in the permit.

13.0 Method Performance

13.1 Method performance (MDL and quality control acceptance criteria) will be determined during the multi-lab validation of this method.

13.2 Total solids duplicate determinations must agree within 10% to be reported for permitting purposes. If duplicate samples do not meet this criteria, the problem must be discovered and the sample must be run over.

14.0 Pollution Prevention

14.2 Pollution prevention details are given in Section 14 of Method 200.7.

15.0 Waste Management

15.1 Waste management details are given in Section 15 of Method 200.7.

16.0 References

16.1 "Standard Methods for the Examination of Water and Wastewater," 18th ed. and later revisions, American Public Health Association, 1015 15th Street NW, Washington, DC 20005. 1-35: Section 1090 (Safety), 1992.

16.2 U.S. Environmental Protection Agency, 1992. Control of Pathogens and Vector Attraction in Sewage Sludge. Publ 625/R-92/013. Office of Research and Development, Washington, DC.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

17.1 Tables containing method requirements for QA/QC will be added after the validation study has been performed.

G EXAMPLE INSTRUMENT CALIBRATION FORM

TETRA TECH

Field Meter Calibration Record

Meter ID	Analyte	Calibration Standard	Pre-Cal Measurement	Post-Cal Measurement	*Pass / Fail	Date	Time	Initials

* - Refer to QAPP (Section 15.1) for calibration parameters and requirements.