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UNIVERSAL PROPULSION COMPANY

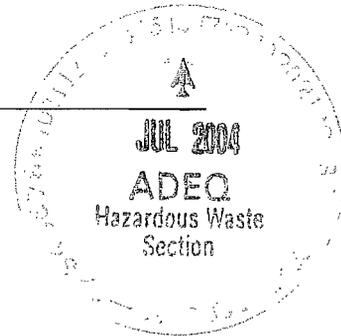
PERMIT ATTACHMENT E  
QUALITY ASSURANCE PROJECT PLAN (2004)  
FINAL PERMIT REV 0

**ATTACHMENT E**

**QUALITY ASSURANCE PROJECT PLAN (2004)**



Universal Propulsion Company  
Goodrich Corporation  
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Phoenix, AZ 85027-7899  
Tel: 623-516-3340  
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July 16, 2004

*Hand Delivered*

Mr. Greg Workman  
Hazardous Waste Section Manager  
Arizona Department of Environmental Quality  
1110 W. Washington Street  
Phoenix, AZ 85007

RE: Quality Assurance Project Plan (QAPP) Revision

Dear Mr. Workman,

The Goodrich Universal Propulsion Company, Inc. (UPCO) located at 25401 North Central Avenue in Phoenix, Arizona is submitting to the Arizona Department of Environmental Quality the attached revision to the Quality Assurance Project Plan (QAPP) submitted on June 11, 2004. Please note that Appendices A-D are not attached, but are exactly the same as the June 11 QAPP.

I certify under penalty of law that this document and all attachments were prepared under my direction or supervision according to a system designed to assure that qualified personnel properly gather and evaluate the information submitted. Based upon my inquiry of the person or persons who manage the system, or those persons directly responsible for gathering the information, the information submitted is, to the best of my knowledge and belief, true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment for knowing violations.

If you have any questions or concerns, please contact Karen Mittleider at 623.516.3340 x2266.

Sincerely,

Christine H. Probett  
President, Aircraft Interior Products

Attachment

cc (w/ attachment): Mr. Bruce Campbell, Arizona State Land Department  
Ms. Karen O'Regan, City of Phoenix Office of Environmental Programs  
Mr. Anthony Orlich, Arizona State Land Department  
Ms. Cynthia Stefanovic, Arizona State Land Department

July 16, 2004



REMEDIAL INVESTIGATION WORK PLAN  
GOODRICH UNIVERSAL PROPULSION COMPANY, INC.

VOLUME II OF II  
QUALITY ASSURANCE PROJECT PLAN  
PHOENIX, ARIZONA



**HARGIS + ASSOCIATES, INC.**



REMEDIAL INVESTIGATION WORK PLAN  
GOODRICH UNIVERSAL PROPULSION COMPANY, INC.  
QUALITY ASSURANCE PROJECT PLAN

PHOENIX, ARIZONA

APPROVALS:

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Hyte Johnson, Goodrich Aircraft Interior Products  
Manager, Remediation Services

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Date

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Hargis + Associates, Inc.  
Project Director

\_\_\_\_\_  
Date

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Michael F. Wiese, Senior Hydrogeologist  
Hargis + Associates, Inc.  
Task Manager

\_\_\_\_\_  
Date

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Jeffery C. Yentes, Senior Hydrogeologist  
Hargis + Associates, Inc.  
Task Manager

\_\_\_\_\_  
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Barbara A. Murphy, Senior Hydrogeologist  
Hargis + Associates, Inc.  
Quality Assurance Manager

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Date

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Greg Workman, Manager, Hazardous Waste Section  
Arizona Department of Environmental Quality

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Date

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Kenyon C. Carlson, Manager  
Quality Assurance/Quality Control Unit  
Arizona Department of Environmental Quality

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Date

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Laboratory Quality Assurance Manager  
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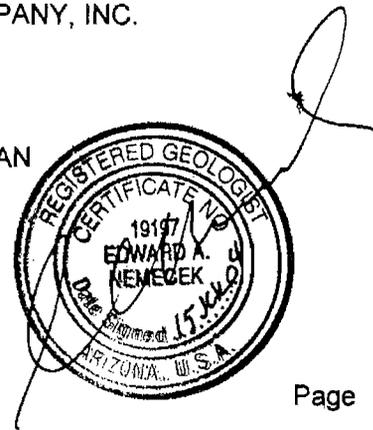
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REMEDIAL INVESTIGATION WORK PLAN  
GOODRICH UNIVERSAL PROPULSION COMPANY, INC.

VOLUME II OF II  
QUALITY ASSURANCE PROJECT PLAN  
PHOENIX, ARIZONA

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- C LABORATORY DOCUMENTATION REQUIREMENTS FOR DATA VALIDATION, QUALITY ASSURANCE PROGRAM, U.S. ENVIRONMENTAL PROTECTION AGENCY, REGION IX, SAN FRANCISCO, CA, DOCUMENT CONTROL NUMBER 9QA-07-97
- D ADDRESSING SPIKE AND SURROGATE RECOVERY AS THEY RELATE TO MATRIX EFFECTS IN WATER, AIR, SLUDGE, AND SOIL MATRICES, ARIZONA DEPARTMENT OF ENVIRONMENTAL QUALITY; OCTOBER 23, 1998
- E PERCHLORATE ANALYTICAL INFORMATION



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REMEDIAL INVESTIGATION WORK PLAN  
GOODRICH UNIVERSAL PROPULSION COMPANY, INC.  
VOLUME II OF II  
QUALITY ASSURANCE PROJECT PLAN  
PHOENIX, ARIZONA

1.0 INTRODUCTION

This Quality Assurance Project Plan (QAPP) has been prepared in support of the Remedial Investigation (RI) activities to be conducted at the Goodrich Universal Propulsion Company, Inc facility (the site), located at the intersection of Central Avenue and Happy Valley Road at 25401 North Central Avenue, Phoenix, Arizona (Figures 1 and 2). This QAPP is submitted pursuant to the request of the Arizona Department of Environmental Quality (ADEQ) (ADEQ, 2004).

The overall objective of the RI is to propose additional investigative work required to complete a remedial investigation. The proposed investigation is based on existing data from previous site characterization activities, data developed during the drilling and sampling of one borehole and two monitor wells (H +A, 2003), and the sampling of up-gradient domestic wells.

1.1 PURPOSE AND SCOPE

This QAPP has been prepared in accordance with U.S. Environmental Protection Agency (EPA) guidelines and requirements (EPA, 1998a and 1998b). The QAPP identifies RI data quality objectives (DQOs) and provides a framework for collecting data that meet the DQOs. The DQOs are qualitative and quantitative statements that identify the minimum level of data quality assurance (QA) necessary to meet the intended uses of the data to be collected. QA is defined as the integrated program designed to ensure that DQOs are met. Quality control (QC) is a component of the QA program and is defined as the routine use of standard procedures to conform to prescribed performance criteria in the monitoring and measurement process. QC procedures are established on the basis of DQOs. The QC procedures contained in this QAPP

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are intended to ensure that project activities are performed in accordance with professional standards, government regulations and guidelines, specific project goals, and DQOs.

This document describes the QA/QC procedures for the collection, identification, preservation, and transport of samples collected during RI activities, the calibration and maintenance of instruments, and the verification, storage, and reporting of project data, including chain-of-custody procedures. Additionally, this document identifies QA project organization and the selected analytical laboratory.

Standard operating procedures (SOPs) have been developed during previous site investigations by Hargis + Associates, Inc (H+A). SOPs are included as appendices to the work plan which accompanies this QAPP. These SOPs include those for surface and subsurface soil sample collection, lithologic logging, monitor well drilling and construction, water level measurements, and groundwater sampling. Proposed work plan activities are to be performed using these SOPs.

1.2 SUPPORTING DOCUMENTS

This QAPP supports activities proposed during RI activities. Other documents to be used in support of project objectives include the following:

- Monitor Well Construction Work Plan, Revision 1 (H+A, 2003)

The Monitor Well Construction Work Plan (plan) was prepared to support the field methods and procedures component of drilling the initial two monitor wells installed at the site. The plan includes: a facility description, a brief summary of previous work performed at the site; a summary of expected hydrogeologic conditions, and a summary of field methods and procedures for monitor well drilling and construction.

- Soil Characterization Work Plan, Storage Magazine Area (H+A, 2004)

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The Soil Characterization Work Plan (plan) includes a facility description, a summary of previous investigations, a description of regional and local hydrogeologic conditions, proposed soil sampling locations, and procedures for soil sampling in the Storage Magazine Area. The plan includes SOPs for lithologic logging and soil sampling.

- RI Work Plan.

The RI Work Plan will be prepared to outline and summarize the methods and procedures required to characterize potential source areas within the site identified in previous reports. The work plan will be supported by supplemental work plans for each phase of the investigation.

- Health and Safety Plan (HSP), (H+A, 2004a)

The HSP is being prepared to outline safety measures to be implemented during the implementation of the activities outlined in the RI Work Plan.

### 1.3 SITE DESCRIPTION

The facility is located at the intersection of Central Avenue and Happy Valley Road at an address of 25401 North Central Avenue, Phoenix, Arizona, approximately 2 miles north of the Deer Valley Airport (Figure 1). The facility is located within the southeast quarter of Section 5, Township 4 North, Range 3 East of the Gila and Salt River Baseline and Meridian. The facility comprises approximately 160 acres and consists of numerous manufacturing and administrative buildings. A security fence surrounds the entire facility and access to the facility is restricted. The facility was initially constructed in 1972.

The facility manufactures solid propellant actuated devices, aircraft ejection seats, aircrew escape systems, stun grenades, gas generators, and other miscellaneous products related to the military/aerospace industry

#### 1.4 PREVIOUS INVESTIGATIONS

The UPCO facility, as part of the RCRA Part B Permit, conducted a RCRA Facility Investigation (RFI) of several solid waste management units (SWMUs) (Figures 1-3) In June 1999, UPCO contracted with SA&B Environmental & Chemical Consultants (SA&B) to conduct the RFI of these SWMUs.

During the period 1999 to 2001, surface and subsurface soil samples were collected and analyzed (SA&B, 1999 and 2001). Soil samples were collected at six SWMUs identified as SWMU 5, 10, 11, 19, 20, and 22. Soil samples were analyzed for selected organic and inorganic constituents as a function of the operations conducted at or near each SWMU.

Concentrations of constituents of potential concern in soil samples obtained from SWMUs 5, 19, 20, and 22 were less than the limits of detection and/or less than the respective State of Arizona residential soil remediation level. No remedial actions are planned for SWMUs 5, 19, 20, and 22.

Elevated concentrations of perchlorate were detected in surface and subsurface soil samples in SWMUs 10 and 11. Concentrations of perchlorate ranged from non-detect to 1,800 milligrams per kilogram (mg/kg) in soil samples from SWMUs 10 and 11. In general, the highest concentrations were found nearest the surface. The vertical and horizontal extent of perchlorate concentrations in soils was delineated using a provisional health based guidance level of 38 mg/kg perchlorate (SA&B, 2001). Further characterization of SWMUs 10 and 11 has been requested by ADEQ (ADEQ, 2003) and is described in a work plan submitted to ADEQ on July 15, 2004.

In December 2003, two monitor wells were drilled and constructed in areas generally down-gradient of the operational areas of the facility (Hargis + Associates, Inc. [H+A], 2003) (Figure 2). Depth to water is approximately 206 to 217 feet below land surface (bls). The wells were developed and initially sampled during the first quarter of 2004.



## 1.5 GEOLOGIC AND HYDROGEOLOGIC CONDITIONS

### 1.5.1 Geologic Conditions

The site is located within the Basin and Range physiographic province (Fenneman, 1931). The Basin and Range physiographic province is characterized by broad, elongate basins and long, narrow mountain ranges resulting from regional block-faulting. Basin and range faulting is the result of extension due to the thinning of the earth's crust. Vertical movement of crustal blocks created mountains on the upthrown side and basins on the downthrown side of regional faults. As time and weathering eroded the mountains, thick sequences of clastic sediments were deposited in the adjoining valleys.

### 1.5.2 Hydrogeologic Conditions

This summary of regional and local hydrogeologic conditions is based on a review of Arizona Department of Water Resources well records, ADEQ file data, hydrogeologic data from the on-site production well and hydrogeologic information and data from published reports compiled by others.

#### 1.5.2.1 Regional Hydrogeologic Conditions

The facility is located in the northeast portion of the West Salt River Valley Sub-basin, very near the boundary with the East Salt River Valley Sub-basin (Reeter and Remick, 1986; Hammett and Herther, 1995). The West Salt River Sub-basin is comprised of a heterogeneous inter-bedded mixture of valley-fill deposits generally surrounded by bedrock outcrops. The sub-basin is bounded on the east by the Union Hills, the Phoenix Mountains and the Papago Buttes. The southern boundary includes South Mountain, the Sierra Estrella Mountains and the Buckeye



Hills. The west boundary consists of the White Tank Mountains and the northern boundary consists of the Hieroglyphic Mountains.

The waterbearing units within the valley-fill deposits are divided based on lithologic characteristics. In descending order from the land surface, the water-bearing units include the upper alluvial unit, the middle fine-grained unit and the lower conglomerate. The primary water-bearing unit in the West Salt River Valley Sub-basin is the upper alluvial unit. The upper alluvial unit ranges in thickness from zero feet near the mountain fronts to more than a 1,000 feet in the interior of the subbasin (Reeter and Remick, 1986).

Depths to groundwater vary within the upper alluvial unit temporally and with location. Generally, groundwater levels are shallowest near the primary surface water courses including the Agua Fria, Salt and Gila Rivers. Groundwater levels generally are deeper as distance from the rivers increases. Groundwater levels are also affected by centers of groundwater pumpage.

Groundwater in the upper alluvial unit generally occurs under unconfined conditions and ranges from a sodium/calcium-bicarbonate water type to a sodium-chloride type. Total dissolved solids concentrations in upper alluvial groundwater range from as low as 200 milligrams per liter (mg/l) in the northern portion of the subbasin to approximately 2,400 mg/l generally along the western extent of the Salt River (Reeter and Remick, 1986).

#### 1.5.2.2 Local Hydrogeologic Conditions

Hydrogeologic data and information for the facility are limited. The following description of hydrogeologic conditions is based on a review of well logs for the existing two facility supply wells, published reports, a brief geologic reconnaissance of the facility and observations and lithologic logging conducted during the drilling of two monitor wells in December 2003.

The northeastern portion of the facility is located adjacent to, and in, the Union Hills. The Union Hills are composed predominately of altered volcanic rocks (Wilson, et al., 1957). Consolidated bedrock is exposed at the land surface in the northeastern portion of the facility. The



consolidated bedrock is overlain by a layer of colluvium, which generally thickens down the topographic gradient to the southwest. The colluvium is comprised of silt- to cobble-sized angular fragments of locally derived rocks. The colluvium likely grades into alluvium (valley fill deposits) toward the southwest corner of the facility. The alluvium consists of silt- to gravel-sized angular to sub-angular fragments of locally derived rock. The majority of the facility is underlain by colluvium and alluvium with bedrock likely underlying these formations at depth. The thickness of the valley fill deposits is estimated as approximately 390 feet in the southwestern portion of the facility.

In August 2003, a depth to water was measured at approximately 208 feet bls in the facility production well. This depth to water was generally consistent with water level data from published reports (Hammett and Herther, 1995). The well is completed in unconsolidated deposits and bottoms in fractured bedrock.

In December 2003, two monitor wells were installed in the southeastern portion of the facility (H+A, 2003). Monitor well UPCO-MW-1 is 240 feet deep and penetrates unconsolidated to semi-consolidated sediments and bedrock. Monitor well UPCO-MW-2 is 250 feet deep and also penetrates unconsolidated to semi-consolidated sediments and bedrock. Depth to water in the monitor wells ranged from approximately 206 to 217 feet bls, which is consistent with water levels in the production well and published reports (Hammett and Herther, 1995).

Based on the topography, surface water drainage direction, published reports, and the recent data from monitor well installations, the general movement of groundwater is to the southwest (Hammett and Herther, 1995).

## 2.0 SCOPE AND OBJECTIVES OF REMEDIAL INVESTIGATION WORK PLAN TASKS

The scope and objectives of the RI activities are defined and detailed in the RI Work Plan (H+A, 2004b). The following activities are included in the QAPP and will be performed as part of the RI:

- Task I – Surface and Subsurface Soil Sampling
- Task II - Drilling, Coring, and Construction of Borings and Monitor Wells
- Task III - Measuring Water Levels and Sampling of Groundwater Monitor Wells

Implementation of the RI Work Plan will follow the review and approval of the RI Work Plan by ADEQ. It is anticipated that field work will commence during the third quarter of 2004.

### 2.1 TASK I – SURFACE AND SUBSURFACE SOIL SAMPLING

The scope of Task I will include collecting surface and subsurface soil samples as part of RI activities as well as when selected monitor wells are drilled. The surface and subsurface soil samples will be analyzed for perchlorate using EPA Methods 300.0MOD/314.0MOD. Selected soil samples may be analyzed for selected metals using EPA Method 6010B. The subsurface soil samples will be collected at approximately 10 foot intervals; at the discretion of the field hydrogeologist, soil sample intervals may be less than 10 feet, because of location-specific variations. The field hydrogeologist will exercise discretion on the basis of interpretations of soil characteristics observed during drilling including changes in lithologic characteristics, color, or other factors that might indicate a difference in chemical composition. Complete descriptions of surface and subsurface soil sampling, field methods, and documentation are presented in the accompanying RI Work Plan and in associated SOPs.

## 2.2 TASK II - DRILLING, CORING, AND CONSTRUCTION OF BORINGS AND MONITOR WELLS

The scope of Task II will include the drilling, coring, and construction of borings and monitor wells at the site. Final monitor well locations and construction details will be selected, and will be based on the results of the previous investigations and consultation with ADEQ.

New monitor wells will be drilled, cored, and constructed using methods and procedures consistent with the previous monitor well drilling activities conducted at the site (H+A, 2003). Complete descriptions of the monitor well drilling, coring, and construction and documentation are presented in the accompanying RI Work Plan and in associated SOPs.

## 2.3 TASK III –SAMPLING OF GROUNDWATER MONITOR WELLS

The scope of Task III will include obtaining well head elevation data, measuring water levels and collecting an initial groundwater sample from each of the newly constructed monitor wells. Groundwater samples will be analyzed for perchlorate using EPA Method 300.0MOD/314.0MOD (see Appendix E). Selected groundwater samples may be analyzed for selected metals using EPA Methods 200.7and/or 200.9. Initial groundwater samples will be analyzed for volatile organic compounds (VOCs) using EPA Method 8260B.

Each newly constructed monitor well will be incorporated into the site quarterly groundwater monitoring program after the initial groundwater sampling event. Complete descriptions of initial groundwater sampling, field methods, and documentation are presented in the accompanying RI Work Plan and the associated SOPs.

### 3.0 PROJECT ORGANIZATION AND RESPONSIBILITY

The project organization chart lists the H+A, ADEQ, and subcontractor personnel responsible for implementation of the RI Work Plan activities (Figure 3). QA activities at the site will be overseen by a QA team comprising the following project personnel: Project Director, Task Managers, QA Managers, and Field Task Managers and the ADEQ Project Hydrogeologist. The QA team is responsible for ensuring that valid measurement data are obtained and for routinely verifying laboratory and field measurement data. The following sections describe the responsibilities of the individual members of the QA team.

#### 3.1 PROJECT DIRECTOR RESPONSIBILITIES

The Project Director is responsible for general project supervision including directing and reviewing the activities of Task Managers, the QA Manager, and the individual Field Task Managers. The Project Director, Mr. Edward A. Nemecek RG, CPG, will directly perform or supervise the performance of the following:

- Coordinate and oversee project activities and data management.
- Approve corrective actions for field and office data management.
- Ensure that data meet project-specific objectives.
- Review data quality verification results and approve database summary reports.
- Act as liaison to Goodrich and ADEQ.

### 3.2 TASK MANAGER RESPONSIBILITIES

The Task Managers will be responsible for ensuring that each individual component of task activities meets overall project objectives and will report to the Project Director. Task Managers may also serve as Field Task Managers. The Task Managers will be Mr. Jeffery C. Yentes and Mr. Michael Wiese; they will directly perform or supervise the performance of the following:

- Ensure that the procedures specified in this QAPP and in the Work Plan are implemented and that all project activities conducted at the site meet stated objectives.
- Determine sampling and analytical strategies with the assistance of the QA team.
- Approve, designate, and monitor corrective action of all field and office activities, as needed.
- Review and approve project documents, data verification results, and database summary reports.
- Communicate with the Project Director regarding task and project status.

ADEQ Project Manager: Overall responsibility for the direction of the scope of work to be performed for the project. Provides final review and approval of documents, reports, plans, schedules, and other communications submitted pursuant to a Task Assignment. Provides coordination of the overall project, and provides consultant overview and direction.

### 3.3 QUALITY ASSURANCE MANAGER RESPONSIBILITIES

The QA Manager is responsible for informing field personnel of the QC practices to be employed prior to field work; performing and overseeing QA/QC functions throughout RI activities; and communicating QA/QC status and requirements to the Project Director and Task



Managers. The QA Manager, Ms. Barbara A. Murphy, will directly perform or supervise the performance of the following:

- Report directly to the Project Director.
- Coordinate QA/QC functions with the Task Managers.
- Review and approve all QA/QC documents pertaining to RI activities.
- Review and approve all modifications to this QAPP, as necessary, and distribute modifications to all parties.
- Coordinate all field sampling efforts with the analytical laboratory.
- Maintain a record of all samples submitted for analysis to the laboratory, the analyses performed, and the final results.
- Ensure that proper sample custody procedures are followed.
- Review chain-of-custody records and sample transmittal documents for completeness.
- Ensure that appropriate field measurement data and analytical laboratory data are entered, stored, maintained, and backed-up in an electronic database management system.
- Perform the verification and validation of the quality of data and review analytical results with project personnel.
- Monitor progress in correcting laboratory deficiencies, if necessary.

ADEQ Project QA Officer: Responsible for review of QA documents (including QAPPs) submitted pursuant to the RI Work Plan. Provides comments and recommendations to the

ADEQ Project Manager regarding appropriate methodologies, reporting limits, sampling and preservation techniques, Data Quality Objectives, and other chemistry related issues. Performs data validation tasks or assigns and supervises ADEQ data validation tasks as requested by ADEQ Project Manager.

### 3.4 FIELD TASK MANAGER RESPONSIBILITIES

Field Task Managers are responsible for overseeing all field activities, for communicating field activities with the Task Manager, and for coordinating all sampling efforts with the QA Manager and the analytical laboratory. The Field Task Manager, to be assigned prior to scheduled field activities, will:

- Contact off-site private property or facility owners and obtain permission to conduct project activities, if required.
- Coordinate field activities with all subcontractors and establish contractual agreements, as necessary.
- Provide training for all sampling personnel, as necessary. Training may include lithologic logging procedures, sample collection procedures, and decontamination procedures. All Field Task Managers and field personnel will be required to be in compliance with applicable health and safety requirements, as well as Occupational Safety and Health Administration training requirements for hazardous waste sites.
- Coordinate all sampling efforts with field personnel and the QA Manager.
- Prepare a sampling memorandum before each sampling event that indicates the sampling methodology; number, type, and size of samples to be collected; and preservation and analytical analysis methods required. The Field Task Manager will review this memorandum with field personnel prior to sampling.



- Designate sampling locations and assign sample identifiers for associated QC samples, including trip blanks, equipment rinsate blanks, and field duplicates.
- Ensure that all field supplies and equipment, including sampling equipment, bottles, labels, custody seals, preservatives, and shipping supplies necessary to properly sample the appropriate media, are available and are in good working order.
- Ensure that field personnel adhere to the procedures documented in this QAPP unless field conditions require project modifications.
- Note any necessary modifications to procedures in the field book.
- Review field notebooks and ensure that all appropriate field data forms are complete and correct.
- Coordinate corrective action, as necessary, for all field activities.

### 3.5 ADEQ PROJECT HYDROGEOLOGIST RESPONSIBILITIES

ADEQ Project Hydrogeologist: Review technical documents, reports, plans, and schedules submitted pursuant to the RI Work Plan. Provides technical comments, recommendations, and professional opinions to the ADEQ Project Manager and ADEQ Project QA Officer.

### 3.6 LABORATORY PROJECT MANAGER RESPONSIBILITIES

Laboratory Project Manager: Ensures laboratory resources are available, reviews final analytical reports produced by the laboratory, reviews and approves QAPP, coordinates scheduling of laboratory analyses, and supervises in-house chain-of-custody procedures.

### 3.7 SPECIALIZED TRAINING, REQUIREMENTS, AND CERTIFICATIONS

All personnel responsible for and involved in the implementation of the RI activities will be thoroughly knowledgeable and experienced in the various aspects of the work to be completed. This knowledge and experience will include, but not be limited to, familiarity with the site geologic and hydrogeologic conditions, laboratory data review and verification, site physical conditions and access, site personnel and contacts, and site health and safety rules, procedures, and protocols.

Subcontractors involved in the implementation of the RI activities will be similarly knowledgeable and experienced. In addition to knowledge and experience, subcontractors will also possess the following minimum requirements:

- Drilling subcontractor – Licensed by the Arizona Department of Water Resources to drill and install monitor wells within the state of Arizona, and duly registered with the Arizona Registrar of Contractors.
- Analytical laboratory – Certified by the Arizona Department of Health Services to perform laboratory analyses within the state of Arizona.

#### 4.0 DATA QUALITY OBJECTIVES FOR WORK PLAN TASKS

DQOs are qualitative and quantitative statements that specify the minimum level of data quality assurance necessary to meet the intended uses of the data to be obtained. DQOs are initially identified during project scoping and are incorporated into the QAPP to provide implementable objectives that ensure that the data obtained are of a quality consistent with their intended uses. EPA DQO guidance was followed where feasible when preparing the DQOs (EPA, 1998a and 1998b). Major data use categories for data obtained are summarized in Table 1. QA objectives are established to provide criteria for evaluating the measurement process to ensure that the resultant data satisfy the DQO established for each activity (Table 2). QA decision makers have previously been identified (Section 3.0).

DQOs will also be used in the development of the RI Work Plan. The RI Work Plan and associated documents, including supplemental work plans, will describe the following:

- Objectives for the various sampling efforts to be conducted.
- Rationale for the selection of sampling locations, number of samples to be collected, analyses to be performed, and the intended use of the data.
- Detailed descriptions of the procedures to be used for sample collection and handling.

The following sections briefly summarize the DQOs for field measurement, sampling, and testing activities at the site. Each section identifies the rationale for the activity, the analytical procedures to be used, if applicable, the intended use of the data, and the QC criteria required to meet each DQO.

#### 4.1 TASK I – SURFACE AND SUBSURFACE SOIL SAMPLING

The DQOs for surface and subsurface soil sampling are to obtain data on the concentration of perchlorate and selected metals in potential source areas, if present (Table 2). Surface soil

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samples will be collected in selected areas of the facility. Subsurface soil samples will be collected during the drilling of soil borings and may be collected during drilling of monitor wells, dependent on location. Monitor well location rationale is discussed in the RI Work Plan and supplemental work plans. The number of surface and/or subsurface soil samples to be collected at each sampling location, soil boring or monitor well location is based on the requirements of the characterization and consultation with ADEQ, and will be presented in the supplemental work plans described in the RI Work Plan. Results of Task I activities, combined with the results of Task II and III, will be used to determine if selected locations at the site are potential sources to the underlying vadose zone and groundwater.

The DQO for this task will be achieved by conforming to SOPs and specific QA objectives by conforming to analytical methods and SOPs in the laboratory, and by applying data verification and data validation procedures to analytical data obtained from laboratory analysis of surface and subsurface soil samples. Specific activities and procedures to be conducted during the subsurface soil sampling are addressed in the RI Work Plan and associated supplemental work plans. Specific procedures to be conducted during laboratory analysis, data verification, and data validation are addressed in this QAPP (Sections 5.0 and 6.0; Tables 3 through 7; Appendices A through D).

4.2 TASK II - DRILLING, CORING, AND CONSTRUCTION OF BORINGS AND MONITOR WELLS

The DQO for drilling, coring, and constructing monitor wells is to provide facilities for sampling groundwater quality representative of the aquifer system present beneath the site. The total number of monitor wells and location rationale is discussed in the RI Work Plan. Results of Task II activities, combined with the results of Tasks I and III, will be used to determine if selected locations at the site are potential sources to the underlying vadose zone and groundwater.

The DQO for this task will be achieved by conforming to SOPs and specific QA objectives for activities associated with this task (Table 2). The procedures for selection/installation and

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sampling of the monitor wells will be the same as previously used for constructing the two existing monitor wells. It is therefore expected that the data collected from these new monitor wells will be consistent with data collected from existing monitor wells. Specific activities and procedures to be conducted during the selection and installation of additional monitor wells are addressed in the RI Work.

#### 4.3 TASK III - GROUNDWATER SAMPLING OF MONITOR WELLS

On the basis of past sampling and analysis performed at the two existing monitor wells, it has been determined that groundwater has been impacted by perchlorate. The DQOs for the groundwater sampling of the newly constructed monitor wells are to obtain information about the concentration levels of nitrate, perchlorate, VOCs, and selected metals; areal and vertical extent of any contamination detected; and potential for contaminant migration, if present in the groundwater and/or overlying soils (Table 2). Initial groundwater samples will be collected after the completion of monitor wells. Monitor well location rationale is discussed in the RI Work Plan. The number of groundwater samples to be collected at each monitor well location is based on the requirements of the characterization and consultation with ADEQ, and is presented in the RI Work Plan. Results of Task III activities, combined with the results of Tasks I and II, will be used to determine if selected locations at the site are potential sources of contaminants to the underlying vadose zone and groundwater.

The DQO for this task will be achieved by conforming to SOPs and specific QA objectives for activities associated with this task, by conforming to analytical methods and SOPs in the laboratory, and by applying data verification and data validation procedures to analytical data obtained from laboratory analysis of groundwater samples. Specific activities and procedures to be conducted during the groundwater sampling are addressed in the RI Work Plan. Specific procedures to be conducted during laboratory analysis, data verification, and data validation are addressed in this QAPP (Sections 5.0 and 6.0; Tables 3 through 7; Appendices A through D).

## 5.0 MEASUREMENT DATA ACQUISITION

This section summarizes SOPs for sample collection and sample custody, as well as QC procedures for field measurements, sample collection, and laboratory analyses to be used during activities at the site. The purposes of these procedures are to ensure proper handling of samples during collection, transportation, storage, and analysis, and to ensure that all field measurements are performed in a manner consistent with the DQOs. Laboratory QC procedures used for the analysis of samples by the fixed analytical laboratory are provided in Appendix A.

### 5.1 SAMPLE COLLECTION

Groundwater and surface and subsurface soil samples will be collected. The types, locations, and number of samples to be collected, procedures for preparation and decontamination of sampling equipment, and methods of waste disposal were determined based on available data and objectives and are provided in the RI Work Plan. The field sampling methodology to be employed and the laboratory analyses required of the sample matrices are also specified.

Samples will be identified, preserved (if necessary), and transported in such a manner that data are representative of the actual site conditions and no information is lost in sample transport. Additional sample handling protocols are presented for groundwater, surface and subsurface soil samples collected at the site in Table 7.

SOPs provided in the RI Work Plan will be followed during the collection of groundwater and soil samples. If specialized equipment is necessary, arrangements will be made or subcontractors will be contacted by the Field Task Manager. Sampling and measurement equipment will be thoroughly checked for proper operation and calibration prior to any field activity.

Field notebooks and copies of field data forms will be reviewed by the Field Task Manager. Field notebooks and field data forms will be retained in the project files. Transmittal letters and chain-of-custody records will be reviewed by the QA Manager for completeness. The analytical

laboratory will notify the QA Manager of sample receipt and will acknowledge receipt of samples on the chain-of-custody record.

## 5.2 SAMPLE DOCUMENTATION AND CUSTODY

Standard sample documentation procedures are established for sampling activities to ensure control of samples during collection, transportation, and storage. The following section addresses the sample documentation and custody procedures for all samples collected.

Sample documentation includes the preparation of sample identification and transmittal documents so that sample identification can be maintained and sample location and disposition can be monitored and controlled. The following sample identification and transmittal documents will be used:

- Sample identification labels
- Chain-of-custody records
- Transmittal letters
- Courier or express mail receipts
- Field data forms
- Bottle custody seals

### 5.2.1 Sample Identification Labels

Pre-printed, adhesive, sample identification labels will be secured to the sample containers by the field sampler. Sample documentation forms and labels will be completed using waterproof ink.

Sample identification labels for soil and groundwater samples sent to a laboratory will contain the following information:

- Sample location/identifier
- Date and time sample was collected
- Analyses to be performed
- Project number
- Sampler initials
- Preservation method used.

### 5.2.2 Chain-of-Custody Records

Official sample custody will be maintained and documented from the time of sample collection to the presentation of analytical results in the final report. The chain-of-custody records will document the transfer or shipment of samples to the analytical laboratory personnel and will detail the analyses requested for each sample.

Fixed laboratory chain-of-custody records will contain the following information:

- Sample location/identifier
- Project code
- Date and time sample was collected
- Project Manager and QA Manager names, telephone number, and fax telephone number
- Names of sampling personnel
- Shipping method used and date
- Sample description
- Sample matrix
- Sample volume and number of containers
- Sample destination
- Preservation method used
- Analyses to be performed
- Special handling procedures.

Erroneous entries on chain-of-custody records will be corrected by drawing a line through the error and entering the corrected information. Corrections will be initialed by the individual making them.

#### 5.2.2.1 Field Custody Procedures

The field sampler, or other designated personnel, will be responsible for sample care and custody from the time of sample collection until the time of sample transferal or shipment to the laboratory. The QA Manager will review each chain-of-custody form to determine whether proper custody procedures were followed during field work and will decide if any corrective action is required.

#### 5.2.2.2 Transfer of Custody and Shipment of Samples

Chain-of-custody records will be used to document transfer of sample custody. When transferring samples, the individuals relinquishing and receiving the samples will sign, date, and note the time on the chain-of-custody records.

Samples will be properly packaged for shipment in accordance with all hazardous materials regulations and will be dispatched to the designated laboratory for analysis with a separate transmittal letter and chain-of-custody record accompanying each shipment. The method of transport, courier name, and other pertinent information will be entered in the transmittal letter and chain-of-custody record accompanying the samples.

The original chain-of-custody record will be sent to the laboratory designated on the chain-of-custody record. Once received at the laboratory, laboratory custody procedures will apply (Section 5.2.2.3).

#### 5.2.2.3 Laboratory Custody Procedures

A laboratory-designated sample custodian will accept custody of the shipped samples upon receipt at the laboratory and will verify that the field identification numbers on the samples match those on the chain-of-custody record. The sample custodian will document, on the chain-of-custody record, the condition of the samples upon receipt and verify that the integrity of the containers has not been compromised. Pertinent information as to shipment, pickup, and courier will be entered in the “Remarks” section of the chain-of-custody record. It is the laboratory’s responsibility to maintain chain-of-custody records throughout sample preparation and analysis. Additional laboratory-specific custody procedures are provided in Appendix A.

#### 5.2.2.4 Field Notebooks and Field Data Forms

A record of sample identification will be maintained on the field data forms. Field data will be compiled in the field notebook. Additionally, field notebooks will include a record of significant events, observations, and measurements made during field investigations, including names of personnel present, site conditions, drilling procedures, sampling procedures, measurement procedures, and calibration records. Field measurements recorded on standardized field data forms will be maintained in the project files.

All field data forms will be signed, dated, and kept as a permanent record. All entries will be made in ink. Erroneous entries on the field data forms will be corrected by drawing a line through the error and entering the correct information. Corrections will be initialed by the individual making them.

### 5.3 QUALITY CONTROL PROCEDURES

QC procedures are developed for field activities and laboratory analyses to ensure that samples are collected and analyzed in a manner consistent with the DQOs. Field and laboratory QC

procedures are prepared for field instrument and equipment calibration, sample collection, field parameter measurements, and laboratory analyses (Tables 2 through 7).

### 5.3.1 Calibration Procedures and Frequency

Field equipment used to perform various measurements will include, at a minimum, an electric sounder for measuring depths to groundwater, a pH meter for measuring water pH, and electrical conductivity (EC) meter for measuring the EC of water, a field thermometer for measuring temperature of groundwater, and an in-line flow meter or stopwatch and calibrated container for measuring well discharge. Field equipment will be calibrated and used to perform the necessary field measurements in a manner such that data are representative of the actual site conditions.

Field equipment will be maintained, calibrated, and operated according to manufacturer guidelines and recommendations. At a minimum, all field equipment will be inspected and calibrated on receipt from a vendor or from another company office. The following guidelines apply to equipment calibration:

- Calibrate all field equipment prior to field activities, including instruments used to measure field water quality parameters, water levels, and monitor well discharge volumes.
- Calibrate the pH meter daily with two buffer solutions of 4.0 and 10.0. This range of buffer solutions will bracket the expected range of pH measurements in groundwater.
- Calibrate the EC meter and the EC standard appropriate for the expected EC values to be measured. Calibrate EC meter prior to the start of each sampling day using EC solutions that provide a midpoint and maximum range based on expected site conditions.

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- Calibrate the electric sounder against a backup sounder at the beginning of each water level data collection event, and record the results in a field notebook.
- Check the accuracy of thermometers against other thermometers prior to field use.
- Calibrate the stopwatch used for well discharge measurements once a year against another stopwatch of a similar type, or return it to the manufacturer for appropriate calibration.
- If the calibration of an instrument cannot be easily checked, either test it against another instrument of a similar type or return it to the manufacturer for appropriate calibration on a quarterly basis at a minimum.

A routine schedule and record of field equipment calibration will be maintained in the field notebook. This will enable the user to document the procedures used in verifying the accuracy of the field equipment.

Sufficient critical spare parts and supplies will be maintained for all field instruments at an easily accessible, on-site storage location to repair or maintain equipment with a minimal impact to field activities. Critical spare parts for field equipment may include:

- pH meter
- pH probe
- pH probe filling solution
- pH calibration/buffer solution
- pH paper
- EC calibration solution
- Thermometer (mercury)
- Thermometer probe
- Batteries for pH and EC meters

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Specific procedures for calibration, operation, and maintenance of laboratory equipment are described briefly by the analytical laboratory in Appendix A.

### 5.3.2 Field Measurements

QC procedures will be implemented for field measurements, including water level, pH, EC temperature, and monitor well discharge volume, to ensure that all field measurements are performed and recorded in a manner consistent with the DQOs. In general, the following steps must be implemented as part of the QC procedures for field measurements:

- Document field equipment maintenance and calibration.
- Establish written SOPs that are accessible.
- Train personnel in all SOPs relating to their assigned tasks.
- Specify professional oversight for various field procedures.
- Maintain well-organized, verified, and accessible data files, including original data and field notes.
- Perform informal, internal peer auditing of work by field personnel and formal auditing by the QA Manager or a designate through interaction with the Project Director.
- Document any corrective action taken in the field notes.

#### 5.3.2.1 Water Level Measurements

Water levels will be measured using calibrated electric water level indicators. Field personnel will check to see that the instruments are properly calibrated prior to use, according to the

procedures outlined previously. Methods and procedures for water level measurement are detailed in the RI Work Plan and associated supplemental work plans.

At each location, the water level will be measured a minimum of two times. The most representative measurement will be determined by the experienced field technician and recorded on the appropriate field data form. Water levels will be measured to the nearest 0.01 foot.

In addition to replicate measurements, the water level data will be compared to nearby measurements obtained at the site. If variations greater than 2 feet exist that cannot be accounted for by local groundwater activities, changes, or trends, alternate equipment may be used to verify the accuracy of the data. The field technician will indicate the method(s) used to measure water levels and any rechecked water level measurements on the field data form.

#### 5.3.2.2 Field Parameters

Measurements for pH, EC, and temperature will be taken during the groundwater sampling events. Field personnel will check to see that the instruments are properly calibrated prior to use, according to the procedures outlined in the respective section of the QAPP. Reference solutions for pH and EC will be prepared and used to properly calibrate the instrument. The pH meter accuracy will be checked prior to use each day. The EC meter accuracy will be checked a minimum of one time at the beginning of each sampling day. If the pH meter is not within  $\pm 0.5$  pH units of the expected value, it will be recalibrated. If the EC meter is not within  $\pm 10$  percent of the expected value, it will be recalibrated.

Field parameter data will be compared to nearby locations. If variations greater than 10 percent exist that cannot be accounted for by changes in field conditions and/or water quality stabilization, the instrument calibration will be checked and recalibrated if needed, and the measurements repeated. If possible, alternate equipment will be used to verify the accuracy of the data. The most representative measurement will be determined by the experienced field technician and will be recorded in the field notebook or on the appropriate field data form.

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All probes and thermometers will be rinsed with distilled water prior to use at a new sampling location. The water sample used for field parameter measurements will be discarded and will not be used to fill sample containers.

#### 5.3.2.3 Well Discharge Measurements

Well discharge rates will be measured during development of each monitor well, during groundwater sampling events. Where discharge is to be measured using a properly calibrated in-line meter or container, QC will be achieved by making two measurements in succession to calculate the discharge rate. If variations greater than 10 percent exist between replicate measurements, additional measurements will be taken. The most representative measurement will be determined by the experienced field technician and will be recorded in the field notebook and/or on the appropriate field data form.

In addition to replicate measurements, the monitor well discharge data will be compared to measurements obtained nearby the location. If variations greater than 10 percent exist that cannot be accounted for by changes in pumping groundwater conditions, the container calibration will be checked and the measurements repeated. If possible, alternate equipment will be used to verify the accuracy of the data.

#### 5.3.3 Sample Collection

QC procedures will be implemented for sample collection to ensure that all groundwater and soil samples are collected in a manner consistent with the DQOs. The Field Task Manager will determine the sampling locations and sample identifiers for QC samples, including duplicate samples, equipment rinse blanks, and trip blanks. This information will be confirmed by the QA Manager and will be contained in the field memorandum issued to the field sampling personnel prior to the sampling event.

The following QC guidelines apply to sample collection:

- Collect one duplicate sample to be analyzed for perchlorate and selected metals for every set of 10 or less surface and subsurface soil or groundwater samples collected. The Field Task Manager will direct the selection of the locations of duplicate sampling so that duplicate samples are collected at different locations as site characterization proceeds.
- Include one equipment rinsate blank containing analyte-free, deionized water for analysis. The equipment rinsate blank will be prepared by field personnel immediately before the last soil or groundwater sample is collected. The purpose of the equipment rinsate blank is to identify any possible contamination associated with soil sample and/or groundwater sample collection using non-dedicated sampling equipment.
- Include one trip blank containing analyte-free, deionized water for analysis in each daily sample shipment containing groundwater samples. The trip blank will be prepared by laboratory personnel immediately prior to initiating the field sampling event. The purpose of the trip blank is to identify any possible contamination associated with shipment of groundwater samples to the analytical laboratory.

QC samples will be identified in the same manner as all other samples so that the laboratory will not be aware of their nature as QC samples. Identifiers will be determined by the Field Task Manager prior to the sampling event and will be indicated on the sampling memorandum.

#### 5.3.4 Laboratory Analysis

Del Mar Analytical, Inc., Phoenix, Arizona (DMA), AZ DHS #AZ0426, is the designated analytical laboratory for soil and groundwater sample analyses. Other qualified analytical laboratories may be designated to perform analyses. Laboratory QA objectives and procedures for DMA are specified in Appendix A. Analytical summaries containing project-specific QC

criteria to be followed by the laboratory for analysis of groundwater and soil are provided (Tables 3 through 7).

#### 5.3.4.1 Laboratory Facilities

Laboratory facility requirements include, but are not limited to, the following:

- The laboratory will have the appropriate equipment available for sample preparation and analysis for the analytical methods requested.
- The laboratory will use reagents and supplies that meet the minimum requirements in the analytical methods.
- All instruments and equipment used for sample analysis will be maintained, calibrated, and operated according to laboratory SOPs, analytical method criteria, and manufacturer guidelines and recommendations.

#### 5.3.4.2 Sample Custody

Laboratory sample custody procedures include, but are not limited to, the following:

- Sample custody is documented from the time samples are received at the laboratory by the sample custodian, throughout the analytical process, and until the samples are disposed.
- Upon receipt at the laboratory, each sample is assigned a unique laboratory identification number that is used to track that sample. The sample identification number will be documented by the laboratory sample custodian on the chain-of-custody record.



#### 5.3.4.3 Laboratory Analytical Procedures

Generalized standard laboratory analytical procedures include, but are not limited to, the following:

- Analyze samples according to the methods specified (Table 7).
- Analyze samples within the holding time required by the analytical method or as requested by the sampling personnel, whichever time period is shorter, according to the objectives of the particular task,.
- Calibrate each instrument used in the analyses prior to sample analysis to ensure that all analyses meet the method requirements.
- Analyze calibration standards and instruments blanks daily to check instrument consistency and performance.
- Analyze one set of calibration standards each 8-hour shift or every 12 hours, as applicable, or whenever a calibration check standard does not meet project-specific acceptance criteria.
- Analyze one set of method blanks daily or per analytical batch of 20 samples or fewer, whichever is more frequent.
- Analyze at least one spike sample with each analytical batch of 20 or fewer samples.
- Analyze at least one duplicate sample or spike duplicate sample with each analytical batch of 20 or fewer samples.
- Compare accuracy and precision from spike and replicate sample analyses to established project-specific QC criteria.

- Maintain performance records to document data quality.
- Use confirmatory methods whenever the identification of an analyte of interest cannot be determined by the main analytical method or when unfamiliar, non-routine samples are analyzed. Confirmatory methods may include analyses by alternate analytical methods as specified by the appropriate methods.
- Routinely determine the limit of detection or method detection limit for each analyte analyzed on each instrument.
- Compounds used to spike samples in groundwater samples collected from on-site and off-site monitor wells are shown in Table 5.

#### 5.3.4.4 Laboratory Reporting

Laboratory reporting procedures include, but are not limited to, the following:

- Review analytical data, laboratory worksheets, and QC records, including spike and duplicate analytical results, on file at the laboratory for future reference.
- Submit analytical laboratory reports to H+A.
- Submit data report package consisting of results sheets from each batch of samples and copies of the instrument or method blank, matrix spike and, matrix spike duplicate (MSD) summary, and the surrogate or internal standard recoveries. The data package includes all relevant sample information, including laboratory identification number; sample identifier; analytical method; date and time of sample collection, extraction, and analysis; dilution factor; and reported detection limits (RDLs). Additionally, the data report package shall include results of the laboratory control sample (LCS) and the laboratory control sample duplicate (LSCD) in accordance with ADEQ policy 0514.000 (Appendix D).

- Type all analytical reports and include a cover letter signed by appropriate laboratory personnel, analytical report sheets for each sample, and QA sample results summaries.

#### 5.3.4.5 Preventive Maintenance

Preventive maintenance includes those activities that must be carried out to minimize downtime of the field and laboratory measurement systems. Specific laboratory preventive maintenance measures are provided by the laboratory in Appendix A. Procedures for preventive maintenance during sampling and field measurement activities include, but are not limited to, the following:

- Calibrate and check field measurement equipment before use.
- Ensure that critical spare parts for instruments are immediately available in case of equipment failure, including electric sounders, extra batteries, buffered solutions, pH and EC meters.
- When practical, ensure that back-up equipment is available. If samples are subcontracted by DMA, DMA shall be held accountable to ensure that all analytical requirements in the QAPP are followed by the subcontractor.
- Ensure that sufficient monitor well construction materials are on hand to account for variability in monitor well completion, as dictated by hydrogeologic conditions.
- Identify and review sampling locations and procedures each day prior to starting field activities.
- Ensure that additional materials for sample collection, including containers, caps, custody seals and chain-of-custody forms are available on site.



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- The pH meter will be recalibrated if periodic pH buffered solution readings vary by more than  $\pm 0.5$  pH units from the pH of the original buffered solution used to calibrate the probe. The integrity of the pH probe and possible degradation of the pH buffered solutions will also be evaluated.
- The EC meter will be recalibrated if periodic checks of its calibration indicate that EC readings vary by more than 10 percent from the concentration of the calibration standard. The integrity of the EC probe and possible degradation of the EC standard solutions will also be evaluated.
- Thermometers will be checked against reference thermometers prior to field activities. Thermometers that vary by more than 0.5 degrees Celsius ( $^{\circ}\text{C}$ ) from the readings of the reference thermometers will be discarded or certified by a National Institute of Standards and Testing calibration source.
- Sampling and decontamination procedures will be reviewed if contaminants are detected in the trip blanks in concentrations exceeding RDLs or documented laboratory contaminant levels.
- Decontamination procedures will be evaluated if contaminants are detected in equipment blanks in concentrations exceeding PQLs.
- Sampling and decontamination procedures will be reviewed if analytical results of field duplicates indicate poor precision.

Laboratory corrective actions will be initiated if analytical results are not provided in a timely manner or are determined to contain inconsistencies during the data quality verification and validation processes. The laboratory will be contacted to discuss corrective action for specific inconsistencies.

At a minimum, the laboratory will adhere to corrective action procedures outlined in Title 40, Code of Federal Regulations, Section 136 or as outlined by EPA (EPA, 1986).

## 6.0 QUALITY ASSURANCE MANAGEMENT

### 6.1 DATA QUALITY MANAGEMENT

The data quality management program is designed to ensure that QC procedures are maintained from data collection through report preparation. Data quality management will be initiated prior to data collection by implementing QC procedures established to ensure that all data are obtained and analyzed in a manner consistent with QA objectives and are representative of the actual site conditions. Laboratory data will be maintained by DMA in accordance with the DMA Laboratory Quality Assurance Manual (Appendix A). Field data will be maintained by H+A for a minimum period of 5 years. The following sections summarize field and laboratory data quality management and verification procedures.

#### 6.1.1 Data Management

Field and laboratory data will be managed as they are obtained and compiled. Field data will be obtained and compiled in field notebooks and/or on the appropriate field data forms. Laboratory data will be compiled in the data report packages. Field and laboratory data will be entered, stored, and maintained in an electronic database. Tables and graphic representations of the data will be prepared based on these data for use in summary reports. Use of these standard data reporting forms and tables will ensure that data are presented consistently. The QA Manager will maintain all copies of field data forms, original transmittal letter, chain-of-custody records, and the laboratory data packages in the project files. A flow chart illustrating the data management process has been provided (Figure 4).



#### 6.1.1.1 Field Data

Field data forms will be established. The Field Task Manager will retain all field notebooks and copies of all field data forms in the project file. These data files will contain original data and field notes. All files will be well-organized, indexed, verified, and accessible.

Field sampling files will be compiled. Field sampling files will include, but are not limited to, the following information:

- Field notes compiled by sampling personnel during the sampling event
- Field data, including entries on water level data and sampling data forms
- Sample documentation forms, including chain-of-custody records, transmittal letters, and courier receipts, if appropriate

Well completion files will be compiled for all newly constructed monitor wells. Well completion files will include, but are not limited to, the following information:

- Drilling and completion report forms
- Lithologic logs
- Schematic well construction diagrams illustrating as-built well construction details
- Field notes compiled by the on-site hydrogeologist during drilling operations
- Field notes compiled by the on-site hydrogeologist during well development and testing operations

#### 6.1.1.2 Analytical Data

Analytical data files will be established for all activities. These data files will be well-organized, indexed, verified, and accessible. Analytical data will include transmittal letters, original chain-of-custody records, and laboratory data packages assembled by the laboratory performing the

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analyses. These laboratory data packages will be provided by the laboratory as hard copy. Analytical data may also be provided on a diskette. Analytical data with corresponding review qualifiers will be entered, stored, and maintained in an electronic database.

Analytical data files will include, but are not limited to, the following information:

- Original chain-of-custody records
- Laboratory analytical reports from all sampling events
- QC sample results, including field duplicates, trip and equipment rinsate blanks
- Data deliverables packages
- Verification and validation forms compiled during data evaluation.

#### 6.1.2 Data Verification and Data Validation

Data generated from sampling events will be verified and validated to determine if they meet project-specific QC criteria. The quality and appropriate use of data obtained will be determined based on the results of routine verification of 100 percent of the data and on the results of validation procedures performed on approximately 10 percent of the soil and groundwater sampling data. SOPs for data verification and data validation are developed to ensure that these activities are performed consistently (Appendix B).

Analytical data generated will be verified for compliance with criteria for precision, accuracy, representativeness, completeness, and comparability (PARCC) parameters. Verification and validation of analytical data will be performed under the supervision of the QA Manager. A qualified independent individual will be responsible for performing data validation. The laboratory will submit analytical results that are supported by sufficient information to enable the reviewer to fully evaluate data quality (EPA, 1997). A copy of the data validation summary will be provided to ADEQ as a component of the investigation report.

The QA Manager will direct the following activities during the analytical verification process:

- Review of chain-of-custody records
- Review of sample holding times
- Review of trip blank and equipment rinsate blank results
- Review of field duplicate sample results
- Review of laboratory reagent blank, spike, and duplicate sample results.

Data verification results will be used to flag questionable analytical results and to assign data qualifiers. The results will also be used as a basis to request revised analytical data reports from the laboratory and to initiate corrective action. In addition, results will be used to determine corrective action for field sampling personnel.

Approximately 10 percent of the samples will be chosen for data validation. Documentation provided by the laboratory for these samples will be sufficient to support Level III analyses and will be consistent with EPA Region IX's Laboratory Documentation Requirements for Data Validation (Appendix C). Data validation is a systematic process of evaluating analytical data against a pre-established set of QC criteria to determine the quality of the data. Data validation packages will be assembled by the laboratory performing the analyses.

The QA Manager will perform, or direct the performance of, some or all of the following activities during the analytical data validation process:

- Review of sample holding times
- Review of initial and continuous calibration procedures and results, and instrument tuning.
- Review of reagent blank, surrogate, spike, spike duplicate or laboratory duplicate, and interference check sample results
- Review of chromatograms, retention times, and acceptance windows
- Review of calculations and documentation procedures
- Review of environmental samples (includes dilutions and reanalysis)
- Review of sample preparation (extraction/digestion logs), and
- Review of laboratory QC check samples, as applicable.

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Data verification and validation procedures are presented in detailed checklists (Appendix B). These checklists are based on procedures outlined by EPA, where applicable. The data verification and validation process is also based on project-specific criteria and selected method-specific criteria specified in the appropriate EPA test methods (EPA, 1986).

The results of data verification and validation, including the activities described above and any data qualified, will be compiled for each sampling event. These results will be kept on file with a memorandum that explains the reasons for data qualifications and the corrective action to be implemented.

The results of data verification and validation will be used in conjunction with other validation criteria to flag questionable analytical results and to assign data qualifiers. The results will also be used as a basis to request revised analytical data reports from the laboratory and to initiate corrective actions.

Following data verification and validation, analytical results and review qualifiers will be entered into the database from analytical data reports provided by the laboratory. The database will be used to ensure that the data are organized and easily accessible. A hard-copy database printout will be double-checked against the original laboratory analytical reports to ensure data entry accuracy.

### 6.1.3 Data Verification Procedures

Throughout the activities, routine procedures will be used to assess PARCC parameters depending on the DQOs for the sampling event. Descriptions of the PARCC parameters to be evaluated during data verification are described in the following sections. In addition to these parameters, the following criteria will be verified as having been met:

- Holding times
- Correct analytical method
- Chain-of-custody criteria and documentation; and
- Minimal reporting requirements.

#### 6.1.3.1 Precision

Precision is a measure of the agreement or reproducibility among replicate measurements (EPA, 1998b). Examination of precision is a measure to evaluate the reproducibility of measurements under a given set of conditions. Precision is expressed as the relative percent difference (RPD) between duplicates of the same sample. Duplicates consist of internal laboratory duplicates and external field duplicates. Internal laboratory duplicates include sample duplicates and/or MSDs, depending on the analytical method. Analytical results from field duplicate samples provide information on the precision of sample collection procedures. Analytical results from laboratory duplicates and laboratory MSDs provide information on laboratory precision. The RPD between duplicate sample results is calculated using the following equation:

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

Where:

RPD = Relative percent difference

D1 = First sample value

D2 = Second sample value (duplicate)

The calculated laboratory and field duplicate RPDs are evaluated and compared to established project-specific precision control limits (Tables 3 through 7). Unacceptable precision values will be noted in the project file. Data associated with unacceptable laboratory precision results will be qualified, and recommendations for corrective action will be discussed with the laboratory and/or field personnel, as appropriate.

### 6.1.3.2 Accuracy

Accuracy is the degree of agreement between a value and an accepted reference or true value (EPA, 1998b). Accuracy can be expressed numerically as the percent recovery (%R) of a spiked sample. A sample spike is prepared in the laboratory by adding a known concentration of one or more chemicals to one sample in each analytical batch. The chemicals spiked are chosen from the list of analytes detectable by the method being evaluated. Analytical results from spiked samples provide data on matrix interferences and method performance.

Accuracy for the analytical measurement system is defined as the %R for a spiked sample. The %R is calculated as follows:

$$P = \frac{(A - B) \times 100}{C}$$

where:

P = %R

A = Measured concentration in spiked sample (sample + spike)

B = Measured concentration in sample

C = Known concentration of spike compound.

The calculated %R results are compared to project-specific and/or EPA-specified accuracy control limits (Tables 3 through 7).

Unacceptable accuracy results will be noted in the project file. Data associated with unacceptable laboratory accuracy results may be qualified, and recommendations for corrective action will be discussed with the laboratory or field personnel, as appropriate.

Accuracy may be qualitatively verified by evaluating blank contamination. Compounds detected in field blanks and laboratory blanks will be evaluated during data verification procedures. Guidelines are established to evaluate the effects of blank contamination on the accuracy of the analytical results of associated field samples (Appendix B). Unacceptable effects of blank

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contamination will be noted in the project file. Data associated with contamination will be noted in the project file. Data associated with unacceptable blank results will be qualified, and recommendations for corrective action will be discussed with the laboratory and/or field personnel, as appropriate.

Equipment rinsate blanks are defined as samples that are obtained by running analyte-free, deionized water through sample collection equipment after decontamination. These samples are used to determine if decontamination procedures are sufficient.

Laboratory blanks are samples made up in the laboratory using analyte-free water and analyzed along with the investigative samples. Laboratory blanks are useful for detecting contamination in the sample handling and analytical processes at the laboratory.

#### 6.1.3.3 Representativeness

Representativeness is the reliability with which a measurement or measurement system reflects the true conditions under investigation. Representativeness is influenced by the number and location of the sampling points, sampling timing and frequency during monitoring events, and field and laboratory sampling procedures (EPA, 1998b).

Representativeness is a qualitative parameter that is addressed by describing sampling techniques and the rationale used to select sampling locations. Sample location selection may be determined based on existing data, instrument surveys, or observations, or may be randomly selected. Data used to select sampling location may include information on site history, the location of operational areas where discharges may have occurred, water level measurements, groundwater and soil sample results, surface water courses, geologic descriptions such as lithologic logs, and interpretations of study area hydrogeologic conditions.

If applicable, and as necessary, data used that were not obtained by H+A will be evaluated against standards outlined in this QAPP for a particular type of sample collection. For example, water levels measured during a previous investigation at a particular monitor well will be

assigned a high level of confidence if the data are accompanied by information on the type of water level measuring device used, the measuring point identification and elevation, pumping status of the measured monitor well, and construction details of the monitor well. If any of this information is missing, the recorded historical water level will be assigned a lower level of confidence and may be rejected for the analysis of historical conditions.

Historical chemical data regarding the nature of soil or groundwater conditions at the site will be similarly evaluated against the standards developed in this QAPP. Unless information is available regarding the date and method of sample collection, the firm that collected the sample, chain-of-custody documentation, the analytical methods employed, and the QA/QC procedures used, the data point will be assigned a low level of confidence.

Historical information regarding subsurface geologic conditions is often obtained from driller's logs. The quality of driller's logs varies from well to well and driller to driller. Each driller's log to be used in interpretive evaluations will be judged on the basis of field experience at the site and on review of existing site-specific literature regarding subsurface conditions.

#### 6.1.3.4 Completeness

Completeness is defined as a comparison of the number of valid data points obtained from a measurement effort to the total number needed to meet the project goals (EPA, 1989). Data completeness incorporates sample loss and data acceptability.

Analytical data completeness is described as the ratio of acceptable analytical results to the total number of results requested. A completeness value of less than 90 percent indicates that corrective action is necessary to limit the number of incomplete or unacceptable results and to avoid similar problems in future sampling events.

Criteria for incomplete or unacceptable results may include water sample containers broken during shipment or at the laboratory and data qualified as unusable during data verification or

data validation procedures. Analytical data completeness is calculated using the following equation:

$$C = \frac{(\textit{number of acceptable results})}{(\textit{total number of requested results})} \times 100$$

where:

C = Percent completeness.

#### 6.1.3.5 Comparability

Comparability is a qualitative parameter that expresses the confidence with which one data set can be compared to another (EPA, 1989). Comparability is dependent on consistency in sampling conditions and on selection of sampling procedures, sample preservation methods, analytical methods, and expressed units of data.

The comparability requirements for field measurement, sampling, and analysis activities are met by complying with SOPs during sample collection and analysis. The RI Work Plan SOPs were consistently implemented throughout H+A conducted previous site investigations and will remain consistent to ensure comparability with historical data sets. Because of the similarity of data collection and analysis methods, data collected during the planned activities will be comparable to data collected during previous site investigations.

## 6.2 QUALITY ASSURANCE REPORTING TO MANAGEMENT

Overall data quality verification results and corrective actions are reported to the Project Director and Task Managers via the QA Manager. Prior to the preparation of the corresponding summary report, the QA Manager informs the Project Director of internal analytical data verification checklist results and recommendations. The QA Manager informs the Project Director and the Task Managers of all corrective actions to be implemented. The Project



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Director informs project staff of any corrective action to be followed. All corrective actions taken are recapitulated in the corresponding summary report.

## 7.0 REFERENCES CITED

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TABLE 1  
MAJOR DATA USE CATEGORIES

SOURCE OF DATA	INTENDED USE OF DATA
Groundwater	Determine the chemical characteristics of groundwater on and in the vicinity of the site.
	Obtain data to determine the concentrations of perchlorate and selected metals in groundwater.
	Determine if high perchlorate/metals concentrations likely exist in groundwater near potential source areas based on the soil data.
	Determine basic aquifer characteristics, including lithologic conditions, horizontal groundwater gradient and direction of groundwater flow.
Surface and Subsurface Soil	Determine the chemical characteristics of subsurface soils in selected site areas.
	Obtain data on the lateral and vertical distribution of potential impacts to surface and subsurface soils in selected site areas.

TABLE 2  
FIELD PROCEDURES AND QUALITY ASSURANCE OBJECTIVES

PROCEDURE	EQUIPMENT CHECK AND/OR CALIBRATION	OPERATIONAL PROCEDURE	PERSONNEL	DATA STORAGE SYSTEM	PRECISION	ACCURACY
Surface and Subsurface Soil Sample Collection	Trowel or Drive sampler	SOP	Hydrogeologist	Hard copy	NA	NA
Monitor Well Drilling and Construction	Pumps, casing	SOP	Field Task Manager, hydrogeologist	Hard copy	NA	NA
Lithologic Logging	Color chart, Hand lens	SOP	Hydrogeologist	Hard copy	NA	NA
Well Discharge	Container/stopwatch, in-line flow meter	SOP	Hydrogeologist, field technician	Hard copy	5 percent of the discharge rate	±10 percent
Water Level Elevation Measurement	Electric water level sounder	SOP and manufacturer instructions for equipment	Field technician	Hard copy	0.01 foot	0.1 foot
Water Sample Collection (excludes determination of electrical conductivity, pH, and temperature)	Pumps, sample bottles, shipping containers, transmittal forms, custody seals, chain-of-custody records, field forms	SOP	Hydrogeologist, field technician	Hard copy	NA	NA
Electrical conductivity	Conductivity meter, field form	SOP and manufacturer instructions for equipment	Hydrogeologist, field technician	Hard copy	±5 uS when scale units are x1	±10 uS when scale units are x1
pH	pH meter, field form	SOP and manufacturer instructions for equipment	Hydrogeologist, field technician	Hard copy	±0.05 unit	±0.5 unit
Temperature	Field thermometer, field form	SOP	Hydrogeologist, field technician	Hard copy	±0.1°C	±0.5°C

SOP = Standard operating procedure

NA = Not applicable

(±) = Plus or minus

uS = Microsiemens

°C = Degrees Celsius

TABLE 3

ANALYTICAL METHODS, DETECTION LIMITS, AND QUALITY CONTROL CRITERIA  
FOR PERCHLORATE AND METALS ANALYSES IN SOIL AND GROUNDWATER SAMPLES

COMPOUND OF CONCERN	EPA METHOD	METHOD DETECTION LIMITS(a) (µg/kg)	LABORATORY REPORTING LIMITS(a) (µg/kg)	PRECISION(a) (RPD as a percentage)	LCSD/LCSD ACCURACY(a) (as a percentage)
SURFACE AND SUBSURFACE SOIL					
Perchlorate	314.0 MOD	8.0	40	15	85-115
Arsenic	6010B	419	5000	20	80-120
Barium	6010B	38	1000	20	80-120
Cadmium	6010B	130	500	20	80-120
Chromium	6010B	482	1000	20	80-120
Lead	6010B	565	5000	20	80-120
Mercury	7471A	2.5	20	15	85-115
Selenium	6010B	722	5000	20	80-120
Silver	6010B	85	500	20	80-120

(a) May change based on internal laboratory studies

EPA = U.S. Environmental Protection Agency  
 RPD = Relative percent difference  
 µg/l = Micrograms per liter  
 µg/kg = Micrograms per kilogram

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TABLE 3 (continued)  
 ANALYTICAL METHODS, DETECTION LIMITS, AND QUALITY CONTROL CRITERIA  
 FOR PERCHLORATE AND METALS IN SOIL AND INITIAL GROUNDWATER SAMPLES  
 Page 2 of 5

ORGANIC COMPOUND	EPA METHOD	METHOD DETECTION LIMITS(a) (µg/l)	LABORATORY REPORTING LIMITS (a) (µg/l)	PRECISION(a) (RPD as a percentage)	ACCURACY(a) (as a percentage)
<b>GROUNDWATER</b>					
Perchlorate	314.0	0.80	4.0	15	85-115
Arsenic	200.7	4.2	50	20	85-115
Barium	200.7	0.40	10	20	85-115
Cadmium	200.7	1.3	5.0	20	85-115
Chromium	200.7	4.8	10	20	85-115
Lead	200.7	5.7	50	20	85-115
Mercury	245.1	0.067	0.20	15	85-115
Selenium	200.7	7.2	50	20	85-115
Silver	200.7	0.90	5.0	20	85-115
<b>VOLATILE ORGANIC COMPOUNDS</b>					
Acetone	8260B	150	750	35	15 - 125
Benzene	8260B	14	50	15	75 - 120
Bromobenzene	8260B	7.7	250	15	75 - 120
Bromochloromethane	8260B	5.3	250	15	75 - 120
Bromodichloromethane	8260B	7.4	100	15	80 - 120
Bromoform	8260B	5.9	250	15	65 - 120
Bromomethane	8260B	11	250	35	25 - 120
2-Butanone (MEK)	8260B	130	500	35	40 - 120

(a) May change based on internal laboratory studies

EPA = U.S. Environmental Protection Agency  
 RPD = Relative percent difference  
 µg/l = Micrograms per liter  
 µg/kg = Micrograms per kilogram

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TABLE 3 (continued)  
 ANALYTICAL METHODS, DETECTION LIMITS, AND QUALITY CONTROL CRITERIA  
 FOR PERCHLORATE AND METALS IN SOIL AND INITIAL GROUNDWATER SAMPLES  
 Page 3 of 5

ORGANIC COMPOUND	EPA METHOD	METHOD DETECTION LIMITS(a) (µg/l)	LABORATORY REPORTING LIMITS (a) (µg/l)	PRECISION(a) (RPD as a percentage)	ACCURACY(a) (as a percentage)
<b>VOLATILE ORGANIC COMPOUNDS (continued)</b>					
n-Butylbenzene	8260B	18	250	15	80 - 120
sec-Butylbenzene	8260B	12	250	15	75 - 125
tert-Butylbenzene	8260B	11	250	15	70 - 135
Carbon Disulfide	8260B	7.4	250	15	50 - 120
Carbon tetrachloride	8260B	5.2	250	15	70 - 120
Chlorobenzene	8260B	7.7	50	15	80 - 120
Chloroethane	8260B	8.5	250	30	20 - 120
Chloroform	8260B	8.3	100	15	80 - 120
Chloromethane	8260B	10	250	20	40 - 120
2-Chlorotoluene	8260B	9.9	250	15	70 - 120
4-Chlorotoluene	8260B	8.6	250	15	75 - 120
Dibromochloromethane	8260B	8.2	100	15	75 - 120
1,2-Dibromo-3-chloropropane	8260B	19	250	35	50 - 130
1,2-Dibromoethane (EDB)	8260B	6.9	100	15	75 - 125
Dibromomethane	8260B	7.7	100	15	80 - 120
1,2-Dichlorobenzene	8260B	9.2	100	15	80 - 120
1,3-Dichlorobenzene	8260B	8.0	100	15	80 - 120
1,4-Dichlorobenzene	8260B	9.4	100	15	80 - 120
Dichlorodifluoromethane	8260B	11	250	35	20 - 120
1,1-Dichloroethane	8260B	6.9	100	15	80 - 120
1,2-Dichloroethane	8260B	6.2	50	15	75 - 120

(a) May change based on internal laboratory studies

EPA = U.S. Environmental Protection Agency  
 RPD = Relative percent difference  
 µg/l = Micrograms per liter  
 µg/kg = Micrograms per kilogram

  
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TABLE 3 (continued)  
 ANALYTICAL METHODS, DETECTION LIMITS, AND QUALITY CONTROL CRITERIA  
 FOR PERCHLORATE AND METALS IN SOIL AND INITIAL GROUNDWATER SAMPLES  
 Page 4 of 5

ORGANIC COMPOUND	EPA METHOD	METHOD DETECTION LIMITS(a) (µg/l)	LABORATORY REPORTING LIMITS (a) (µg/l)	PRECISION(a) (RPD as a percentage)	ACCURACY(a) (as a percentage)
<b>VOLATILE ORGANIC COMPOUNDS (continued)</b>					
1,1-Dichloroethene	8260B	7.5	250	15	65 - 120
cis-1,2-Dichloroethene	8260B	9.2	100	15	75 - 120
trans-1,2-Dichloroethene	8260B	8.4	100	15	70 - 120
1,2-Dichloropropane	8260B	7.3	100	15	80 - 120
1,3-Dichloropropane	8260B	8.4	100	15	80 - 120
2,2-Dichloropropane	8260B	7.7	100	15	50 - 120
1,1-Dichloropropene	8260B	6.9	100	15	80 - 120
cis-1,3-Dichloropropene	8260B	8.8	100	15	80 - 120
trans-1,3-Dichloropropene	8260B	6.4	100	15	80 - 120
Ethylbenzene	8260B	8.0	100	15	80 - 120
Hexachlorobutadiene	8260B	77	250	15	65 - 150
2-Hexanone	8260B	100	500	35	50 - 120
Iodomethane	8260B	25	100	15	75 - 120
Isopropylbenzene	8260B	9.8	100	15	75 - 125
p-Isopropyltoluene	8260B	13	100	15	70 - 135
Methylene chloride	8260B	60	500	20	70 - 120
4-Methyl-2-pentanone (MIBK)	8260B	150	500	30	50 - 135
Methyl-tert-butyl Ether (MTBE)	8260B	12	250	15	75 - 120
Naphthalene	8260B	67	100	25	45 - 165
n-Propylbenzene	8260B	11	100	15	70 - 130
Styrene	8260B	9.0	100	15	80 - 125

(a) May change based on internal laboratory studies

EPA = U.S. Environmental Protection Agency  
 RPD = Relative percent difference  
 µg/l = Micrograms per liter  
 µg/kg = Micrograms per kilogram

  
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TABLE 3 (continued)  
 ANALYTICAL METHODS, DETECTION LIMITS, AND QUALITY CONTROL CRITERIA  
 FOR PERCHLORATE AND METALS IN SOIL AND INITIAL GROUNDWATER SAMPLES  
 Page 5 of 5

ORGANIC COMPOUND	EPA METHOD	METHOD DETECTION LIMITS(a) (µg/l)	LABORATORY REPORTING LIMITS (a) (µg/l)	PRECISION(a) (RPD as a percentage)	ACCURACY(a) (as a percentage)
<b>VOLATILE ORGANIC COMPOUNDS (continued)</b>					
1,1,1,2-Tetrachloroethane	8260B	8.5	250	15	80 - 120
1,1,2,2-Tetrachloroethane	8260B	11	100	35	60 - 125
Tetrachloroethene	8260B	11	100	15	80 - 120
Toluene	8260B	6.8	100	15	80 - 120
1,2,3-Trichlorobenzene	8260B	60	250	15	55 - 160
1,2,4-Trichlorobenzene	8260B	30	250	15	75 - 140
1,1,1-Trichloroethane	8260B	4.4	100	15	75 - 120
1,1,2-Trichloroethane	8260B	9.6	100	15	75 - 120
Trichloroethene	8260B	11	100	15	80 - 120
Trichlorofluoromethane	8260B	7.8	250	35	25 - 120
1,2,3-Trichloropropane	8260B	10	500	25	60 - 130
1,2,4-Trimethylbenzene	8260B	9.7	100	15	75 - 120
1,3,5-Trimethylbenzene	8260B	10	100	15	75 - 125
Vinyl acetate	8260B	10	1200	35	25 - 130
Vinyl chloride	8260B	4.4	250	35	10 - 120
Xylenes, Total	8260B	18	150	15	80 - 120

(a) May change based on internal laboratory studies

EPA = U.S. Environmental Protection Agency  
 RPD = Relative percent difference  
 µg/l = Micrograms per liter  
 µg/kg = Micrograms per kilogram

  
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TABLE 5

## SPIKING COMPOUNDS FOR ANALYSES

EPA METHOD	INITIAL CALIBRATION
6010B Surface and Subsurface Soil Samples	Arsenic, Barium, Cadmium, Chromium, Lead, Selenium and Silver
7471A Surface and Subsurface Soil Samples	Mercury
314.0MOD Surface and Subsurface Soil Samples	Perchlorate
200.7 Groundwater	Arsenic, Barium, Cadmium, Chromium, Lead, Selenium and Silver
245.1 Groundwater	Mercury
314.0	Perchlorate
8260B Initial Groundwater Samples	Complete analyte list (See Table 3)

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TABLE 6  
 SURROGATE COMPOUNDS WITH QUALITY CONTROL CRITERIA  
 FOR ANALYSES

EPA METHOD	SURROGATE COMPOUNDS	ACCURACY(a) (percent)
6010B Surface and Subsurface Soil Samples	N/A	N/A
314.0MOD Surface and Subsurface Soil Samples	N/A	N/A
7471A Surface and Subsurface Soil Samples	N/A	N/A
200.7 Groundwater	N/A	N/A
314.0 Groundwater	N/A	N/A
245.1 Groundwater	N/A	N/A
8260B Initial Groundwater	1,2-Dichloroethane-d4 Dibromofluoromethane Toluene-d8 4-Bromofluorobenzene	64-119 71-109 78-107 75-108

(a) May change based on internal laboratory studies

EPA=U.S. Environmental Protection Agency

**TABLE 7**
**HANDLING PROTOCOL FOR SOIL AND GROUNDWATER SAMPLES**

ANALYTE (EPA Method)	SAMPLE CONTAINER	SAMPLE VOLUME	PRESERVATION METHOD	MAXIMUM HOLDING TIME
6010B Surface and Subsurface Soil Samples	Brass Sleeve / Glass Jar	100g	None	180 days
314.0MOD Surface and Subsurface Soil Samples	Brass Sleeve / Glass Jar	100g	Cool, 4°C	28 days
7471A Surface and Subsurface Soil Samples	Brass Sleeve / Glass Jar	100g	None	28 days
200.7 Groundwater	500 ml Poly	100 ml	HNO <sub>3</sub>	180 days
314.0 Groundwater	500 ml Poly	100 ml	Cool, 4°C	28 days
245.1 Groundwater	500 ml Poly	100 ml	HNO <sub>3</sub>	28 days
8260B Initial Groundwater	Two 40-ml vials	40 ml	Cool to 4°C	14 days

EPA=U.S. Environmental Protection Agency  
 g=Grams  
 °C=Degrees Celsius  
 ml=Milliliter  
 HCl=Hydrochloric acid

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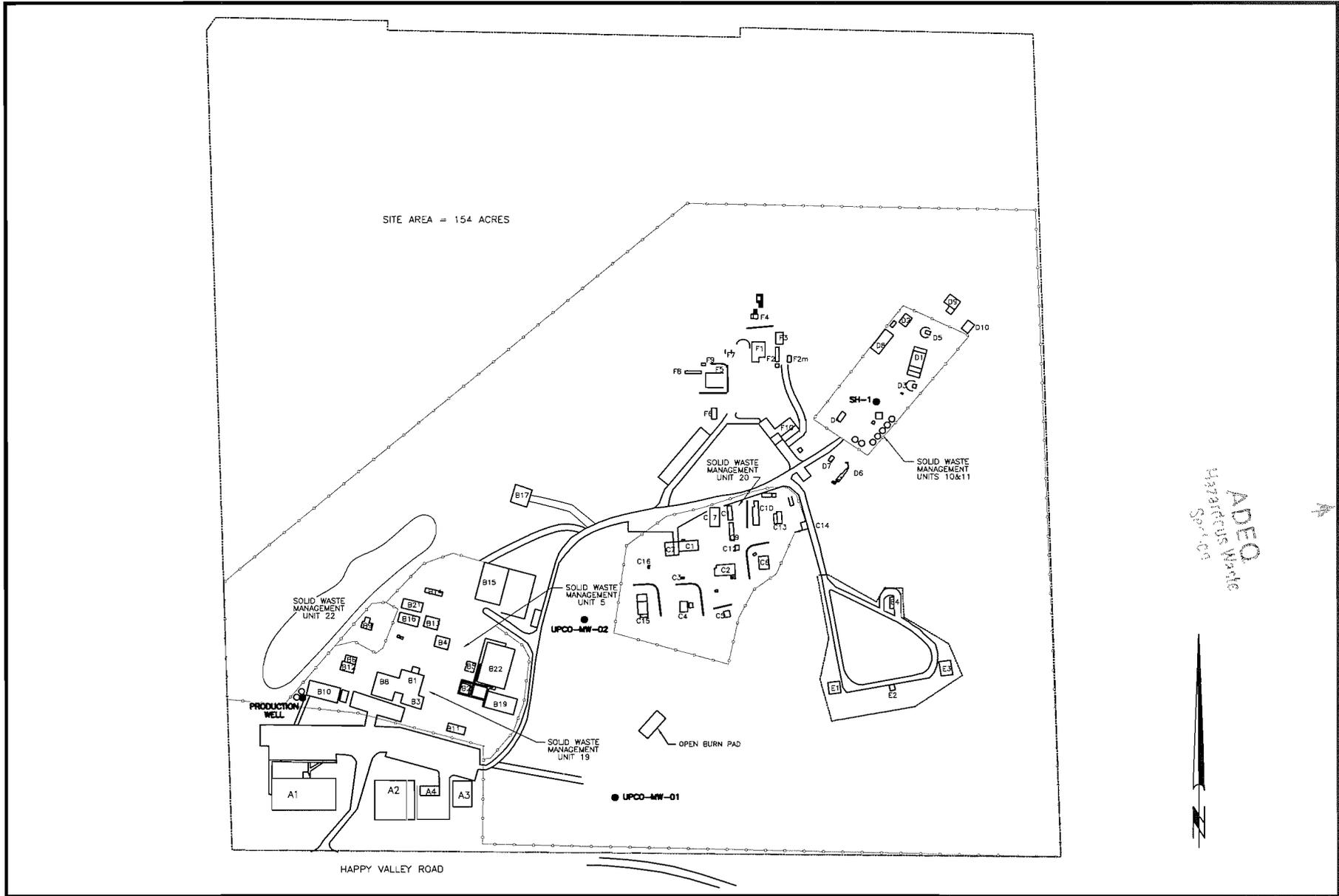
**TABLE 8**
**REPORT DISTRIBUTION LIST**

REPORT TITLE:                   **QUALITY ASSURANCE PROJECT PLAN  
GOODRICH UNIVERSAL PROPULSION COMPANY, INC.  
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NUMBER OF REPORTS SENT	REPORT SENT TO	NUMBER OF REPORTS SENT	REPORT SENT TO
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1	Edward A. Nemecek RG, CPG HARGIS + ASSOCIATES, INC. 1640 South Stapley Drive, Suite 124 Mesa, Arizona 85204 Phone: (480) 345-0888	3	Greg Workman Manager Hazardous Waste Section ARIZONA DEPARTMENT OF ENVIRONMENTAL QUALITY 1110 West Washington Street Phoenix, AZ 85007 Phone: (602) 771-4103
1	Michael Wiese HARGIS + ASSOCIATES, INC. 1640 South Stapley Drive, Suite 124 Mesa, Arizona 85204 Phone: (480) 345-0888	1	Kenyon C. Carlson Quality Assurance/Quality Control Unit ARIZONA DEPARTMENT OF ENVIRONMENTAL QUALITY 1110 West Washington Street Phoenix, AZ 85007 Phone: (602) 771-4866
1	Jeffery C. Yentes HARGIS + ASSOCIATES, INC. 1640 South Stapley Drive, Suite 124 Mesa, Arizona 85204 Phone: (480) 345-0888	1	Elizabeth Wueschner Laboratory Quality Assurance Manager DEL MAR ANALYTICAL 9830 South 51 <sup>st</sup> Street Suite B-120 Phoenix, AZ Phone: (480) 785-0043



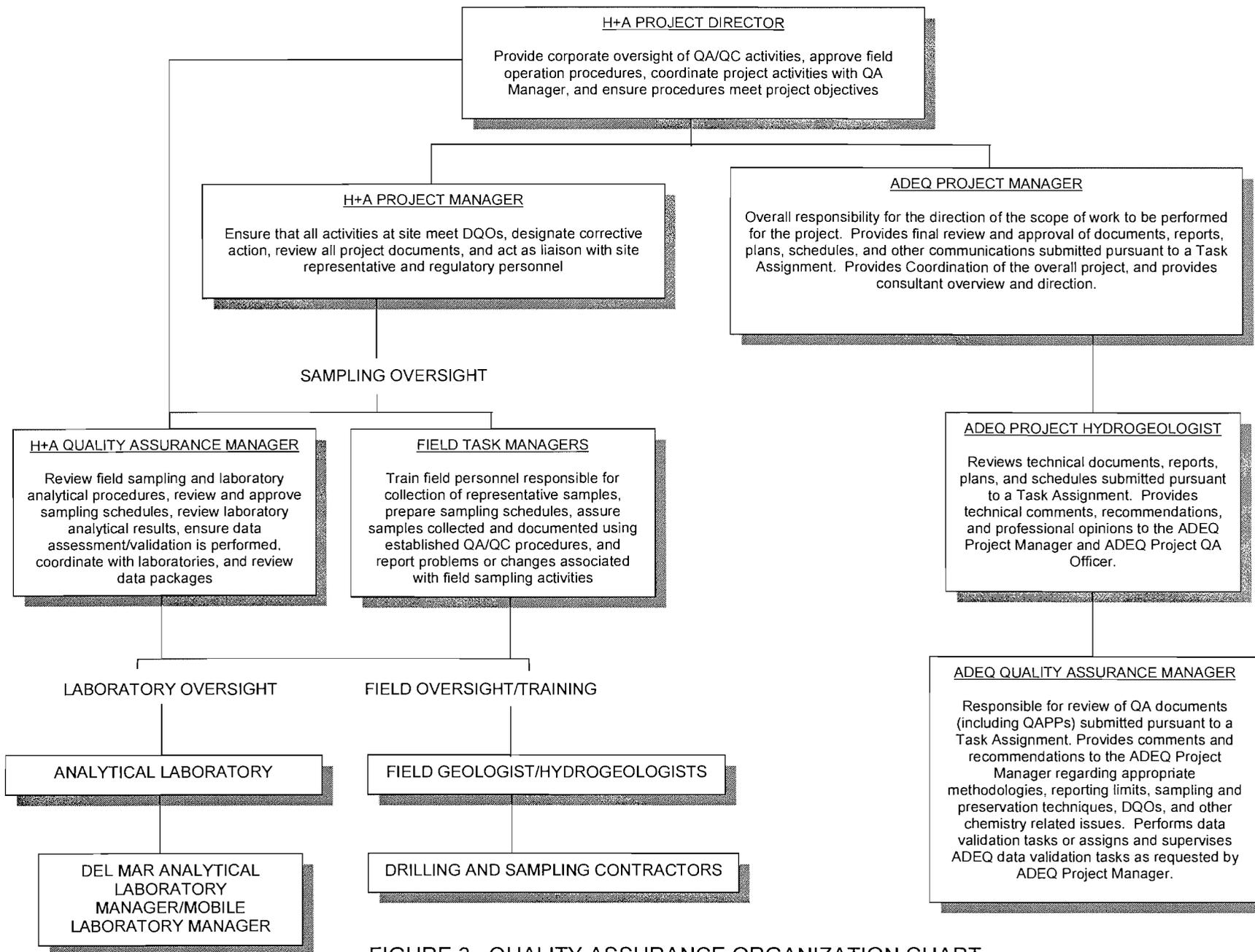
FIGURE 1 FACILITY LOCATION



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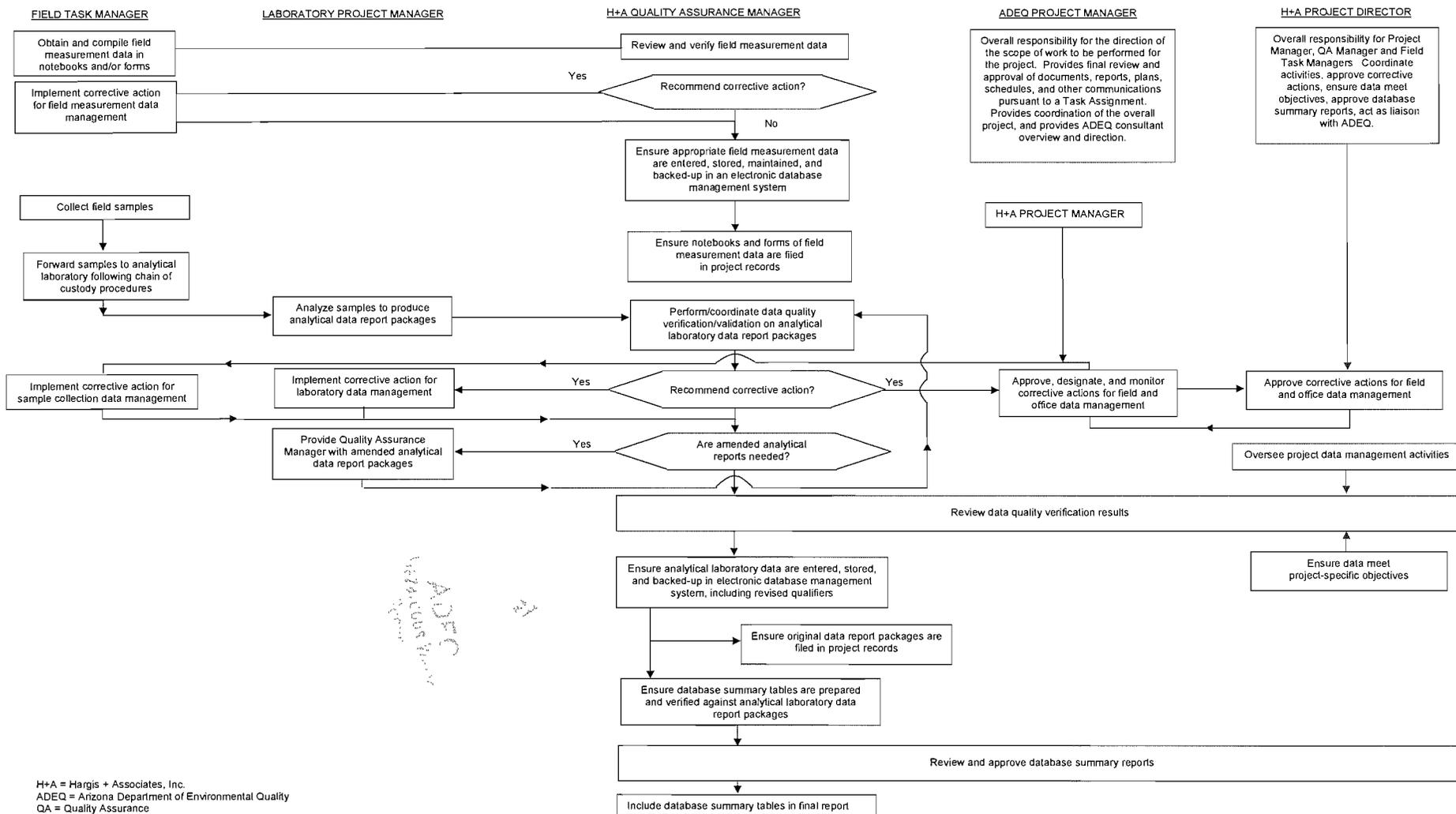


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FIGURE 3. QUALITY ASSURANCE ORGANIZATION CHART

**ADEQ PROJECT QA OFFICER**

Responsible for review of quality assurance documents (including QAPPs) submitted pursuant to a Task Assignment. Provides comments and recommendations to the ADEQ Project Manager regarding appropriate methodologies, reporting limits, sampling and preservation techniques, Data Quality Objectives, and other chemistry and laboratory related issues. Performs data validation tasks or assigns and supervises ADEQ data validation tasks as requested by ADEQ Project Manager.



*Handwritten note:* ADEQ  
 H+AQAM

H+A = Hargis + Associates, Inc.  
 ADEQ = Arizona Department of Environmental Quality  
 QA = Quality Assurance

FIGURE 4. DATA MANAGEMENT PROCESS FLOWCHART

APPENDIX B

STANDARD OPERATING PROCEDURES  
FOR DATA VERIFICATION AND DATA VALIDATION

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APPENDIX B  
STANDARD OPERATING PROCEDURES  
FOR DATA VERIFICATION AND DATA VALIDATION

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## APPENDIX B

### STANDARD OPERATING PROCEDURES FOR DATA VERIFICATION AND DATA VALIDATION

#### 1.0 GENERAL STATEMENT

Chemical quality data for groundwater samples analyzed using U.S. Environmental Protection Agency (EPA) Methods 200.7 and 300.0MOD/314.0MOD and surface and subsurface soil samples analyzed using EPA Methods 6010B and 300.0MOD/314.0MOD will be reviewed during data verification and data validation activities to determine the quality of the data and to assess its use according to the data quality objectives established for the specific field activity. These standard operating procedures (SOPs) have been prepared to ensure that data verification and data validation activities are performed in a consistent manner.

The general procedures used in data verification and data validation efforts are similar. Data validation differs from data verification in the comprehensiveness of the analytical package for review, the degree to which raw analytical data from the analytical laboratory are scrutinized, and the exclusion of site hydrogeologic data and historical trends during data evaluation. Data verification procedures will be performed on all analytical data collected as part of routine project activities. Data validation will be performed on 10 percent of soil samples and initial groundwater samples as specified in this Quality Assurance Project Plan (QAPP).



## 2.0 DATA VERIFICATION PROCEDURES

Data verification procedures include evaluation of the following categories of support documentation associated with analytical data:

- Sample holding times
- Preservation procedures
- Analytical methods and data reporting
- Trip blanks, field blanks and laboratory method blanks
- Matrix spike and matrix spike duplicate analysis
- Laboratory control sample (LCS) and laboratory control sample duplicate (LCSD) analysis
- Surrogate recovery
- Field duplicate analysis
- Data trending.

Standard procedures will be used to perform routine data verification of chemical quality data reported by the laboratory and to assign EPA data qualifiers (Table B-1). Data verification will be performed using hard copy laboratory reports. After data verification activities have been completed, a memorandum summarizing the results will be prepared.

### 2.1 HOLDING TIMES

A comparison will be made between the sampling date and the date of laboratory analysis for each sample submitted to the laboratory. The analytical results for samples identified as exceeding the required holding time will be qualified as estimated with the EPA qualifier "UJ" or "J" and will be documented in the summary memorandum.

## 2.2 ANALYTICAL METHODS AND DATA REPORTING

The laboratory report will be checked against the sample chain-of-custody record to verify that appropriate analytical results were reported for all groundwater and surface and subsurface soil samples submitted and that the analytical methods requested in sample documentation were used by the laboratory. Instances of requested analyses not included in the laboratory report, due to occurrences such as breakage in the laboratory, misidentification of samples, missing or incomplete analyses, or use of incorrect analytical methods, will be documented in the summary memorandum.

## 2.3 TRIP BLANKS, EQUIPMENT RINSATE BLANKS AND LABORATORY METHOD BLANKS

The hard copy laboratory reports will be reviewed to determine whether any analytes analyzed were detected in any of the trip blanks, equipment rinsate blanks, and laboratory method blanks associated with the sampling event and analysis procedures. The results of this analysis will be documented in the summary memorandum. If an analyte analyzed was detected in a blank sample, the following procedures will be performed to identify data subject to qualification:

- Compile a list of blank samples in which analytes were detected, including method of analysis, analyte concentration, batch number of water used to prepare the blank, if available, dates of blank sample collection and analysis, and specific laboratory instrument used for blank sample analysis, if applicable.
- For analyte detections in trip, equipment rinsate, and laboratory method blanks, review the hard copy laboratory reports for all initial groundwater samples from the same quality control batch as the blank sample. Review laboratory reports and identify all detections of the analyte in all associated samples using the same analytical method. Compile a list of identified initial groundwater sample analytical results for qualification.
- Assign data qualifiers to the compiled list(s) of results as follows:



If the concentration of the analyte in the sample is non-detect, the data are acceptable.

If the concentration of the analyte in the sample is detected, but is less than or equal to five times the blank concentration, qualify the data with the EPA qualifier "J".

If the concentration of the analyte in the sample is greater than five times the blank concentration, the data are acceptable.

- Document the review of blank samples and list data qualified in the summary memorandum.

#### 2.4 MATRIX SPIKE AND MATRIX SPIKE DUPLICATE ANALYSIS

Matrix spike (MS) and matrix spike duplicate (MSD) recovery data from samples in the laboratory report will be compared with the acceptable range of percent recovery for each analyte, as specified in the applicable QAPP. If an MS or MSD recovery percentage is outside the acceptance criteria, the following procedures will be used to identify data subject to qualification:

- Compile a list of analyte MS or MSD recoveries that are outside the acceptable percent recovery limits, along with sample identifiers and date of spike sample analysis.
- Review the analytical reports to identify all samples analyzed for the same analyte, for the same analytical method, and within the same analytical batch. Compile a list of identified analytical results for qualification, including all less than detection limit results.
- Assign data qualifiers to the compiled list(s) of results as follows:

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TABLE 4

ACCEPTANCE CRITERIA FOR INSTRUMENT CALIBRATION

EPA METHOD	ACCEPTANCE CRITERIA	
	INITIAL CALIBRATION	CONTINUING CALIBRATION
6010B Surface and Subsurface Soil Samples	$r \geq 0.995$	$\pm 10\%$
314.0MOD Surface and Subsurface Soil Samples	$r \geq 0.995$	$\pm 10\%$
7471A Surface and Subsurface Soil Samples	$r \geq 0.995$	$\pm 10\%$
200.7 Groundwater samples	$r \geq 0.995$	$\pm 10\%$
314.0 Groundwater Samples	$r \geq 0.995$	$\pm 10\%$
7471A Groundwater Samples	$r \geq 0.995$	$\pm 10\%$
8260B Initial Groundwater Samples	RSD $\leq 15\%$ or ( $r^2 \geq 0.99$ ) ( $r \geq 0.995$ )	$\pm 20\%$

RSD = Relative standard deviation

( $\leq$ ) = Less than or equal

( $\geq$ ) = Greater than or equal to

r = Correlation coefficient

- An analyte concentration that is much larger than the spike concentration will reduce the accuracy of the spike recovery. The LCS/LCSD recovery will be used instead to assign a data qualifier.
- If both the MS and MSD are significantly (i.e., 25%) outside acceptance limits and the LCS/LCSD recovery are acceptable, then the sample analyte may be estimated as follows:
  - If both are greater than the upper limit
    - and the sample analyte is non-detect, then it is acceptable.
    - and the sample analyte is detected, then it is qualified as estimated with the EPA qualifier “J”.
  - If both are less than the lower limit OR one is less than and one is greater than:
    - and the sample analyte is non-detect, then it is estimated with the EPA qualifier “UJ”.
    - and the sample analyte is detected, then it is estimated with the EPA qualifier “J”.

## 2.5 LABORATORY CONTROL SAMPLE AND LABORATORY CONTROL SAMPLE DUPLICATE ANALYSIS

LCS and LCSD data in the laboratory report will be compared with the acceptable range of percent recovery for each analyte, as specified in the applicable QAPP. If a LCS/LCSD spike recovery percentage is outside the acceptance criteria, the following procedures will be used to identify data subject to qualification:

- Compile a list of laboratory control sample spike recoveries that are outside the acceptable percent recovery limits, along with sample identifiers and date of spike sample analysis.

- Review the analytical reports to identify all samples analyzed for the same analyte, for the same analytical method, and within the same analytical batch. Compile a list of identified analytical results for qualification, including all less than the detection limit results.
  
- Assign data qualifiers to the compiled list(s) of results as follows:
  - If both are greater than the upper limit
    - and the sample analyte is non-detect, then it is acceptable.
    - and the sample analyte is detected, then it is qualified as estimated with the EPA qualifier “J”.
  
  - If both are less than the lower limit OR one is less than and one is greater than:
    - and the sample analyte is non-detect, then it is estimated with the EPA qualifier “UJ”.
    - and the sample analyte is detected, then it is estimated with the EPA qualifier “J”.
  
- Document the review of LCS/LCSD samples and list data qualified in the summary report.

## 2.6 SURROGATE RECOVERY

Surrogate recovery data in the laboratory report will be compared with the acceptable range of percent recovery for each surrogate, as specified in the applicable QAPP. If a surrogate recovery percentage is outside the acceptance criteria, the following procedures will be used to identify data subject to qualification:

- Compile a list of surrogate recoveries that are outside the acceptable percent recovery limits, along with sample identifiers and date of sample analysis.

- Review the analytical reports to identify all associated analytes analyzed. Compile a list of identified analytical results for qualification, including all less than the detection limit results.
  
- Assign data qualifiers to the compiled list(s) of results as follows:
  - If the surrogate recovery is greater than the upper limit
    - and the sample analyte is non-detect, the sample analyte is acceptable.
    - and the sample analyte is detected, the sample analyte is estimated with the EPA qualifier "J".
  
  - If the surrogate recovery is less than the lower limit
    - and the sample analyte is non-detect, the sample analyte is estimated with the EPA qualifier "UJ".
    - and the sample analyte is detected, the sample analyte is estimated with the EPA qualifier "J".
  
- Document the review of surrogate recovery data and list data qualified in the summary memorandum.

## 2.7 FIELD DUPLICATES

The analytical results for field duplicate samples will be tabulated and RPDs for each analyte will be computed. Instances in which an analyte was detected in only one sample and not in its duplicate sample will be identified and an approximate RPD will be calculated by substituting the analytical detection limit for the less than detection limit result in the RPD formula. The calculated RPDs will be compared to the historical RPDs compiled for field duplicates for the project. If field duplicate analysis for an analyte exceeds the acceptable RPD for the analyte, the concentrations of the analyte detected in the original and associated duplicate samples are subject to further review based on additional data for the site, as described below (Section 2.9).

Based on the outcome of this review, the EPA qualifier “J” may be assigned to the original and/or the duplicate analytical result for the analyte. The results of the duplicate sample review, including rationale for assigning data qualifiers will be included in the summary memorandum.

## 2.8 DATA TRENDING

Each newly constructed monitor well will be incorporated into the site quarterly groundwater monitoring program after initial groundwater sampling. All groundwater quality data for a particular sampling event will be compared to previous chemical quality data collected at that same location, if possible, to accomplish the following: 1) screen field duplicate results that have RPDs greater than the historical data or acceptance criteria to identify data that may have to be qualified; and 2) identify any analytical results that may require qualification for which no field and/or laboratory quality control problem was identified during the verification process. This additional review is necessary to alert the user to data that are not representative of the site.

Review of previous analytical results for samples collected from a particular site may include one or all of the following:

- Review of long-term and/or short-term chemical quality hydrographs for all analytes analyzed at the sampling location.
- Review of chemical quality hydrographs for other sampling locations in the same and adjacent hydrogeologic units in the immediate vicinity of the sampling location evaluated.
- Review of maps showing areal distribution of the concentrations of the analyte in the same hydrogeologic unit.
- Review of water level hydrographs, water level contour maps, and pumpage records from nearby production wells.

- Review of historical surface water records and investigation of sources of potential recharge to groundwater systems in the area of the sampling location.

Individuals familiar with the hydrogeological conditions at the site will evaluate this information and identify a list of data that may require qualification. This list will be reviewed by the Quality Assurance (QA) Manager prior to assignment of data qualifiers. Laboratory personnel may be contacted during the review process to ensure that the data subject to review were correctly reported. Field duplicate sample results identified as having unacceptable RPDs and determined to be out of trend will be qualified with the EPA qualifier "J". Analytical results with no associated quality control problem may be assigned the EPA qualifier "J". This would include a concentration of the sample subject that is approximately one order of magnitude higher or lower than the expected concentration of the analyte at the sampling location and is clearly outside the historical water quality trends at the site; a concentration for an analyte not previously detected at the site; or a lack of detection of an analyte that is routinely detected at the site. The results of the review of data based on trend analysis will be documented in the summary memorandum.

### 3.0 DATA VALIDATION PROCEDURES

Data validation will be performed according to EPA guidelines using method-specific information regarding instrument calibration and type and frequency of quality control checks (EPA, 1996), and using project-specific precision, accuracy, and project-required detection limits included in the applicable QAPP. Data validation procedures include evaluation of the following categories of support documentation associated with chemical quality data:

- Sampling holding times
- Analytical methods and data reporting
- Gas chromatograph performance (as applicable)
- Initial and continuing instrument calibrations
- Trip blanks, equipment rinsate blanks and laboratory method blanks
- Laboratory method blanks
- Surrogate recovery
- Matrix spike recovery and matrix spike duplicate analysis
- Analyte identification and analyte quantitation.

The validation procedures will be used to assign EPA data qualifiers to groundwater and surface and subsurface soil data obtained at the site (Table B-1). Data validation will be performed using data packages prepared by the laboratory in accordance with EPA guidelines (EPA, 1997).

#### 4.0 CORRECTIVE ACTION

Corrective actions may be required at any point in the data verification or data validation process. Problems with laboratory or field quality control data or analytical results should be relayed as soon as possible by H+A to the Laboratory Manager. The laboratory will be instructed to check raw data and computations, as necessary, to identify any problems due to data transposition, reported units of measurement, or calculation errors. The laboratory may be instructed to re-run a partial sample if sample holding time limits have not been exceeded. The laboratory will issue an amended hard-copy analytical report if any previously reported data are found to be in error. If major quality control problems are identified during data validation or data verification procedures, the QA Manager may request that additional samples be collected from a sample location for laboratory analysis.



## 5.0 REPORTING

The QA Manager will review the list of all data to be qualified and will approve data qualifiers. Analytical results found to be satisfactory based on the data verification/validation process will have a clear EPA Qualifier field in the database.

Qualifiers assigned to the EPAQualifier field, with the exception of "U", will appear in tables summarizing the results of the analyses. H+A uses a less than sign (<), to indicate that an analyte was not detected and, therefore, EPA's "U" qualifier will not be used.



6.0 REFERENCES CITED

United States Environmental Protection Agency (EPA), 1996. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. Third Edition, Update III. SW-846; December 1996.

\_\_\_\_\_, 1997. Laboratory Documentation Requirements for Data Validation. Quality Assurance Program, U.S. EPA Region IX, San Francisco, CA; Document Control No. 9QA-07-97.

APPENDIX E

PERCHLORATE ANALYTICAL INFORMATION

**METHOD 314.0**

**DETERMINATION OF PERCHLORATE IN DRINKING WATER USING ION  
CHROMATOGRAPHY**

Revision 1.0

November 1999

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## METHOD 314.0

### DETERMINATION OF PERCHLORATE IN DRINKING WATER USING ION CHROMATOGRAPHY

#### 1. SCOPE AND APPLICATION

- 1.1 This method covers the determination of perchlorate in reagent water, surface water, ground water, and finished drinking water using ion chromatography.
- 1.2 The single laboratory reagent water Method Detection Limit (MDL, defined in Section 3.16) for the above analyte is listed in Table 1. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample and the specific instrumentation employed.
  - 1.2.1 In order to achieve comparable detection limits, an ion chromatographic system must utilize suppressed conductivity detection, be properly maintained, and must be capable of yielding a baseline with no more than 5 nanosiemen (nS) noise/drift per minute of monitored response over the background conductivity.
- 1.3 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.
- 1.4 When this method is used to analyze unfamiliar samples for perchlorate, anion identification should be supported by the use of a laboratory fortified matrix sample. The fortification procedure is described in Section 9.4.1.
- 1.5 Users of the method data should identify data quality objectives prior to analysis. Users of the method must demonstrate the ability to generate acceptable results, using the procedures described in Section 9.0.
- 1.6 This method specifies an IC column and analytical conditions which were determined to be the most effective for the widest array of sample matrices. Other IC procedures have been written which incorporate similar columns and conditions, such as hydroxide based mobile phases, low hydrophobicity IC columns, and measurement by suppressed conductivity detection.<sup>1-5</sup> During the development of this method, these other procedures, as well as the columns and conditions outlined in this method, were concurrently investigated with comparable results for test matrices with moderate levels of common inorganic background anions. These findings were consistent with those of the Inter-Agency Perchlorate Steering Committee, Analytical Subcommittee's Report,<sup>6</sup> published in 1998, which reported on the results of an interlaboratory validation of

these other Ion Chromatographic Methods. The columns and conditions identified in this method were recommended since they bore the greatest tolerance for the highest levels of common inorganic anion interference.

## 2. SUMMARY OF METHOD

- 2.1 A 1.0 mL volume of sample (see Note), is introduced into an ion chromatograph (IC). Perchlorate is separated and measured, using a system comprised of an ion chromatographic pump, sample injection valve, guard column, analytical column, suppressor device, and conductivity detector.

**NOTE:** This large sample loop (1.0 mL) can be made using approximately 219 cm (86 inches) of 0.03 inch i.d. PEEK tubing. The exact volume is not critical since all standards and samples will use the same sample loop. However, the volume should be verified to be within 5% of this volume by weighing the sample loop empty, filling the loop with deionized water and re-weighing the loop. The volume can then be approximated by assuming the density of water is 1.0 mg/uL.

## 3. DEFINITIONS

- 3.1 ANALYSIS BATCH -- A sequence of samples, which are analyzed within a 30 hour period and include no more than 20 field samples. An Analysis Batch must also include all required QC samples, which do not contribute to the maximum field sample total of 20. The required QC samples include:
- Instrument Performance Check Standard (IPC)
  - Laboratory Reagent Blank (LRB)
  - Initial Calibration Check Standard (ICCS)
  - Laboratory Fortified Blank (LFB)
  - Continuing Calibration Check Standard (CCCS), when the batch contains more than 10 field samples
  - End Calibration Check Standard (ECCS)
  - Laboratory Fortified Matrix (LFM)
  - Either a Field Duplicate, a Laboratory Duplicate or a duplicate of the LFM
  - (if pretreated samples are included in batch) Pretreated LRB
  - (if pretreated samples are included in batch) Pretreated LFB
  - (if pretreated samples are included in batch) Pretreated LFM, for each pretreated matrix.

**NOTE:** Every field sample analysis, including both diluted and pretreated field samples, but excluding any LFM or duplicate field sample analysis which qualify as QC samples, must be applied to the maximum of 20 total field samples permitted in an analysis batch.

- 3.1.1 A field sample(s), included in the analysis batch, can be reanalyzed following the ECCS provided the 30 hr time limit for the analysis batch has not expired. The laboratory can reanalyze that sample(s) but must initially conduct a second ICCS before the reanalysis and an ECCS after the final reanalysis. The ECCS must be completed within the 30 hr window.
- 3.2 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution(s) or stock standard solutions. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.
- 3.3 INITIAL CALIBRATION STANDARDS -- A series of CAL solutions used to initially establish instrument calibration and develop calibration curves for individual target anions (Section 10.2).
- 3.4 INITIAL CALIBRATION CHECK STANDARD (ICCS) -- A CAL solution, which is analyzed initially, prior to any field sample analyses, which verifies the previously established calibration curve. The concentration for the initial calibration check standard MUST be at or below the MRL (Section 3.17) level.
- 3.5 CONTINUING CALIBRATION CHECK STANDARDS (CCCS) -- A CAL solution which is analyzed after every tenth field sample analyses, not including QC samples, which verifies the previously established calibration curve and confirms accurate analyte quantitation for the previous ten field samples analyzed. The concentration for the continuing calibration check standards should be either at a middle calibration level or at the highest calibration level (Section 10.3.2).
- 3.6 END CALIBRATION CHECK STANDARD (ECCS) -- A CAL solution which is analyzed after the last field sample analyses which verifies the previously established calibration curve and confirms accurate analyte quantitation for all field samples analyzed since the last continuing calibration check. The end calibration check standard should be either the middle or high level continuing calibration check standard (Section 10.3.2).
- 3.7 FIELD DUPLICATES (FD) -- Two separate samples collected at the same time and place 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.
- 3.8 INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) -- A solution containing a specific concentration of perchlorate and other test substances (namely chloride, sulfate and carbonate) used to evaluate the performance of the instrument system with respect to a defined set of criteria.

- 3.9 LABORATORY DUPLICATE (LD) -- Two sample aliquots (LD1 and LD2), taken in the laboratory from a single sample bottle, and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated specifically with the laboratory procedures by removing variation contributed from sample collection, preservation and storage procedures.
- 3.10 LABORATORY FORTIFIED BLANK (LFB) – An aliquot of reagent water, or other blank matrix, to which a known quantity of perchlorate is 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.
- 3.11 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) – An aliquot of an environmental field sample to which a known quantity of perchlorate is 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 result (when compared to the result for the LFB). The background concentrations of perchlorate, in the sample matrix, must be initially determined in a separate aliquot and the measured value in the LFM corrected for this background concentration.
- 3.12 LABORATORY REAGENT BLANK (LRB) – An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, filtration and reagents that are used with other samples. The LRB is used to determine if perchlorate or other interferences are present in the laboratory environment, the reagents, or the apparatus.
- 3.13 LINEAR CALIBRATION RANGE (LCR) – The concentration range over which the instrument response is linear.
- 3.14 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.
- 3.15 MATRIX CONDUCTIVITY THRESHOLD (MCT) – The highest permitted conductance of an unknown sample matrix, measured prior to conducting the analysis, which is used to determine when sample matrix dilution or pretreatment is required. The conductance of a sample matrix is proportional to the common anions present in the matrix (which contribute to the level of total dissolved solids [TDS]) which can greatly affect the integrity of this analysis. The value for this threshold is dependant on the conditions, hardware, and state of the hardware employed. Consequently, this threshold is not method defined and must be determined by the individual analytical laboratory during the Initial Demonstration of Capability (IDC) and confirmed in each analysis batch using the Instrument Performance Check (IPC) Solution. Matrix

conductivity is measured in microsiemens/cm (uS/cm) or microMhos/cm (uMhos/cm) which are considered equivalent terms.

- 3.16 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.<sup>7,8</sup>
- 3.17 MINIMUM REPORTING LEVEL (MRL) – The minimum concentration that can be reported as a quantitated value for a target analyte in a sample following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.
- 3.18 PEAK AREA TO HEIGHT RATIO (A/H) – The ratio of the peak area divided by the peak height which is used as a tool to monitor analytical performance. This ratio is used to establish and monitor the MCT and represents an objective means of assessing analytical performance when analyzing high conductivity matrices. A gradual distortion of the baseline is typically observed in the retention time window for perchlorate as the matrix conductivity increases (consistent with elevated levels of common anions) which will more significantly influence peak height relative to the influence on peak area. As the distortion of the baseline increases, this ratio increases, and the integrity of the measured perchlorate will be compromised.
- 3.19 PROFICIENCY TESTING (PT) or PERFORMANCE EVALUATION (PE) SAMPLE -  
- A certified solution of method analytes whose concentration is unknown to the analyst. Often, an aliquot of this solution is added to a known volume of reagent water and analyzed with procedures used for samples. Often, results of these analyses are used as part of a laboratory certification program to objectively determine the capabilities of a laboratory to achieve high quality results.
- 3.20 QUALITY CONTROL SAMPLE (QCS) – A solution of method analytes of known concentrations that 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.
- 3.21 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing perchlorate which is either prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.
- 3.22 TOTAL DISSOLVED SOLIDS (TDS) -- Both organic and inorganic constituent which are dissolved in a sample matrix and are not removed by particulate filtration.

#### 4. INTERFERENCES

- 4.1 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 baselines in an ion chromatogram. These interferences can lead to false positive results for the target analyte as well as reduced detection limits as a consequence of elevated baseline noise.
- 4.2 Interferences can be divided into three different categories: direct chromatographic coelution, where an analyte response is observed at very nearly the same retention time as the target anion; concentration dependant coelution, which is observed when the response of higher than typical concentrations of the neighboring peak overlap into the retention window of the target anion; and, ionic character displacement, where retention times may significantly shift due to the influence of high ionic strength matrices (high mineral content or hardness) overloading the exchange sites in the column and significantly shortening target analyte's retention times.
- 4.2.1 A direct chromatographic coelution may be solved by changing columns, eluent strength, modifying the eluent with organic solvents (if compatible with IC columns), changing the detection systems, or selective removal of the interference with pretreatment. Sample dilution will have little to no effect. The analyst **MUST** verify that these changes do not induce any negative affects on method performance by repeating and passing all the QC criteria as described in Section 9.
- 4.2.2 Sample dilution may resolve some of the difficulties if the interference is the result of either concentration dependant coelution or ionic character displacement, but it must be clarified that **sample dilution will alter your Minimum Reporting Limit (MRL)** by a proportion equivalent to that of the dilution. Therefore, careful consideration of project objectives should be given prior to performing such a dilution. An alternative to sample dilution, may be dilution of the eluent as outlined in Section 11.2.6.
- 4.2.3 Pretreatment cartridges can be effective as a means to eliminate certain matrix interferences. With any proposed pretreatment, the analyst must verify that the target analyte is not affected by monitoring recovery after pretreatment (additional pretreated LFM requirement see Section 11.1.4.6) and that no background contaminants are introduced by the pretreatment (additional pretreated LRB requirement see Sections 9.3.1.1 and 11.1.4.2). With advances in analytical separator column technology which employ higher capacity anion exchange resins, the need for these cartridges has been greatly reduced.

- 4.2.3.1 Extreme caution should be exercised in using these pretreatment cartridges. Artifacts are known to leach from certain cartridges which can foul the guard and analytical columns causing loss of column capacity indicated by shortened retention times and irreproducible results. Frequently compare your calibration standard chromatograms to those of the column test chromatogram (received when the column was purchased) or use calibration chromatograms generated when the column was initially installed, to insure proper separation and similar response ratios between the target analytes are observed.
- 4.2.3.2 If LRB background problems are encountered in the retention time window for perchlorate when these pretreatment cartridges have been employed, increase the initial reagent water rinse of the cartridge to approximately five times the volume specified by the manufacturer.
- 4.3 Sample matrices with high concentrations of common anions such as chloride, sulfate and carbonate can make the analysis problematic by destabilizing the baseline in the retention time window for perchlorate. This is evidenced by observing a protracted tailing following the initial elution of the more weakly retained anions (chloride, carbonate, and sulfate) which extends into the perchlorate retention time window. These common anion levels can be indirectly assessed by monitoring the conductivity of the matrix. Consequently, all sample matrices must be monitored for conductivity (Section 11.1.2) prior to analysis. When the laboratory determined Matrix Conductivity Threshold (MCT, see Section 9.2.8) is exceeded, procedures incorporating sample dilution and/or pretreatment must be performed as specified in Sections 11.1.3 and 11.1.4, respectively.
- 4.4 All reagent solutions (eluent, external water for ASRS suppressor, etc...) used by the instrument must be filtered through no larger than a 0.45 um nominal pore size membrane or frit to remove particulates and prevent damage to the instrument, columns and flow systems. Sample filtration must also be employed on every sample prior to analysis. This applies not only to field samples but also to the laboratory reagent blank (LRB) and laboratory fortified blank (LFB). The LRB and LFB samples function as controls and must be filtered to confirm no bias is attributable to the filtration.<sup>5</sup> Filter the samples through a membrane or frit with no larger than a 0.45 um nominal pore size. Syringe mounted, cartridge type, filters work well. Filters specifically designed for IC applications should be used.
- 4.5 Close attention should be given to the potential for carry over peaks from one analysis which will effect the proper detection of perchlorate in a second, subsequent analysis. It is the responsibility of the user to confirm that no late eluting peaks have carried over into a subsequent analysis thereby compromising the integrity of the analytical results.

## 5. 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 specifically listed below in Section 5.3 for hazardous materials.
- 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. Additional references on laboratory safety are available.<sup>9-12</sup>
- 5.3 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS.
- 5.3.1 Sodium Hydroxide (NaOH), used in the preparation of the eluent is considered caustic.

## 6. EQUIPMENT AND SUPPLIES

- 6.1 Ion chromatograph (IC) -- Analytical system complete with eluent reservoirs, an ion chromatographic pump, injection valves, both guard and analytical separator columns, suppressor, conductivity detector, and computer based data acquisition system.
- 6.1.1 Anion guard column -- Dionex AG16 4 mm (P/N 55377), or equivalent. This column functions as a protector of the separator column. If omitted from the system, the retention times will be shorter.
- 6.1.2 Anion separator column -- Dionex AS16, 4 mm (P/N 55376), or equivalent (see Sections 6.1.2.1 - 6.1.2.2). The AS16, 4 mm column using the conditions outlined in Table 1 produced the separations shown in Figures 1 through 4.
- 6.1.2.1 The development of this method included investigations into the performance of alternate 4 mm IC guard and analytical separator columns which have been used for the IC analysis of perchlorate and are specified in procedures external to the U.S.EPA.<sup>1-5</sup> These alternate guard /separator columns included the Dionex AG5 / AS5 and the Dionex AG11 / AS11. The AG5 / AS5 is currently specified in the standard operating procedure (SOP) for the IC analysis of perchlorate by the State of California, Department of Health Services.<sup>1,5</sup> The AG11 / AS11 is used by several commercial labs conducting IC analysis for perchlorate and is recognized by California as an

acceptable alternate to the AG5 / AS5.<sup>2-4</sup> A multilab validation study included both of these analytical columns and indicated comparable results could be attained.<sup>6</sup> In U.S.EPA studies, both the AG5 / AS5 and the AG11 / AS11 performed well for reagent water and simulated drinking water samples with low to moderate common anion levels but as these levels increased, performance began to diminish for both columns. The AG16 / AS16 columns could tolerate much higher levels of these common anions and therefore it is recommended in this method as the column of choice. A summary of the results of examining these three columns for simulated matrices with various common anion levels is presented in Table 4.

6.1.2.2 Any alternate, equivalent column must be characterized as hydrophilic or conversely, must be rated as having low to very low hydrophobicity.<sup>4</sup> This is one characteristic that is consistent for the AS5, AS11 and AS16 analytical separator columns. This requirement for low hydrophobicity is to allow the efficient, reproducible and symmetrical band elution of polarizable anions, such as perchlorate. If the perchlorate analysis is attempted on a hydrophobic column, such as those typically used for the analysis of common anions,<sup>13</sup> poor performance will result due to very asymmetric, tailing peaks. Using a middle to high calibration standard, conduct a typical analysis. Any alternate column must be capable of yielding symmetrical peak elution for this perchlorate response as demonstrated by yielding a Peak Gaussian Factor of between 0.80 and 1.15 using the following equation,

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where,

$W(1/2)$  is the peak width at half height, and

$W(1/10)$  is the peak width at tenth height.

**NOTE:** Values for  $W(1/2)$  and  $W(1/10)$  can be attained through most data acquisition software.

6.1.3 Anion suppressor device -- The data presented in this method were generated using a Dionex Anion Self Regenerating Suppressor (4 mm ASRS, ULTRA, P/N 53946). An equivalent suppressor device may be utilized provided comparable conductivity detection limits are achieved and adequate baseline stability is attained as measured by a combined baseline drift/noise of no more than 5 nS per minute over the background conductivity. Proper suppressor

performance is essential to analytical data reproducibility and sensitivity of the conductivity detector.

6.1.3.1 The ASRS was set to perform electrolytic suppression at a current setting of 300 mA using the external water mode. External water was delivered to the suppressor directly from a pressurized source at a flow rate of 5 mL/min

6.1.3.2 If pretreated samples (Section 11.1.4), or sample matrices which contain appreciable concentrations of transition metal cations (e.g., Fe or Al) are frequently analyzed, cationic components may bind to the suppressor membrane and over time effect suppressor performance. If the instrument begins to have problems with reduced peak response or asymmetrical perchlorate peaks, the suppressor membranes should be cleaned. As a quick and easy cleaning step, the manufacturer's ASRS "Quickstart" procedure for installing a new ASRS should be followed.<sup>14</sup> If this procedure does not correct the problem, follow the manufacturer's recommended cleaning procedure for removing metal contaminants.<sup>15</sup>

6.1.4 Detector -- Conductivity cell (Dionex CD20, or equivalent) capable of providing data as required in Section 9.2.

6.2 Data Acquisition System -- The Dionex Peaknet Data Chromatography Software was used to generate all the data in Tables 1 through 4. Other computer based data systems may achieve approximately the same performance but the user should demonstrate this by the procedures outlined in Section 9.

6.3 Conductivity Meter -- Used to monitor sample matrix conductance which is directly related to the common anion levels in a matrix and used to determine if sample pretreatment is required. At a minimum, this meter should be capable of measuring matrix conductance over a range of 1 - 10,000 uS/cm.

6.4 Analytical balance -- Used to accurately weigh target analyte salt for stock standard preparation ( $\pm 0.1$  mg sensitivity).

6.5 Top loading balance -- Used to accurately weigh reagents such as sodium hydroxide solution in the preparation of eluents ( $\pm 10$  mg sensitivity).

6.6 Weigh boats -- Plastic, disposable - for weighing eluent reagents.

6.7 Micro beakers -- Plastic, disposable - used during sample preparation.

- 6.8 Syringes -- Plastic, disposable, 10 mL - used during sample preparation.
- 6.9 Pipets -- Pasteur, plastic or glass, disposable, graduated, 5 mL and 10 mL.
- 6.10 Bottles -- High density polyethylene (HDPE) or glass, amber or clear, 30 mL, 125 mL, 250 mL. For sampling and storage of calibration solutions. Stability studies presented by the Interagency Perchlorate Steering Committee for Analytical Methods <sup>6</sup> and confirmed at the EPA (see Table3A), indicate perchlorate is neither photoreactive nor prone to adsorption to the walls of either HDPE plastic or glass bottles.
- 6.11 Particulate filters -- 0.45 micron syringe filters, specifically designed for IC applications (Gelman IC Acrodisc, PN 4485, or equivalent). These cartridges are used to remove particulates from the sample matrix while loading the sample manually or if the autosampler employed does not filter the sample during loading.
- 6.12 Matrix pretreatment cartridges in the barium form -- (Dionex OnGuard-Ba cartridges, PN 046072, or equivalent.) These cartridges are conditioned according to the manufacturer's directions and are used to reduce the matrix levels of sulfate.
- 6.13 Matrix pretreatment cartridges in the silver form -- (Dionex OnGuard-Ag cartridges PN 039637, or equivalent.) These cartridges are conditioned according to the manufacturer's directions and are used to reduce the matrix levels of chloride.
- 6.14 Matrix pretreatment cartridges in the hydrogen form -- Dionex OnGuard-H cartridges (PN 039596) or equivalent. These cartridges are conditioned according to the manufacturer's directions and are used to reduce cations in the sample matrix. This protects the analytical column by removing silver which has leached from the Ag cartridge and may indirectly minimize the effect of carbonate by removing the cationic counter ion.

## **7. REAGENTS AND STANDARDS**

- 7.1 Reagent water -- Distilled or deionized water 17.8 Mohm or better, free of the anions of interest. Water should contain particles no larger than 0.20 microns.
- 7.2 Eluent solution -- 50 mM sodium hydroxide (NaOH, [CASRN 1310-73-2]), dissolve 8.0 grams of 50% (W/W) sodium hydroxide in reagent water to a final volume of 2.0 L. **NOTE:** This eluent solution is specific to the columns listed in Table 1. Any alternate columns will likely have unique and specific conditions identified by the manufacturer.
  - 7.2.1 Solutions of NaOH are very susceptible to carbonate contamination resulting from adsorption of carbon dioxide from the atmosphere. This contamination will result in poor reproducibility of perchlorate retention times, elevated

instrument background conductivity, and increased baseline noise/drift. Consequently, exposure to the atmosphere should be minimized by storing these eluent solutions in sealed reservoirs under low pressure (3 to 5 psi) helium. In addition, these solutions should be regularly prepared and held for no more than 5 days. When refilling the eluent reservoir, completely replace old eluent solution by emptying the old eluent, rinsing the reservoir with reagent water, and refilling with the freshly prepared eluent solution. With this eluent, the suppressed conductivity detector background signal should be between 2 - 5 uS.

7.2.2 This eluent solution must be purged for 10 minutes with helium prior to use. This effectively removes dissolved gases which may form micro bubbles in the IC, compromising system performance and adversely effecting the integrity of the data. Alternatively, an in-line degas apparatus may be employed.

7.2.3 A system or apparatus which automatically generates the hydroxide eluent (Dionex EG40, or equivalent) is an acceptable alternative to physically preparing this hydroxide eluent.

7.3 Perchlorate stock standard solution, 1000 mg/L (1 mg/mL) – A stock standard solution may be purchased as a certified solution or prepared from ACS reagent grade, sodium salt as listed below. (NOTE: Sodium perchlorate represents a molar weight fraction of 81.2 % perchlorate anion)

7.3.1 Perchlorate ( $\text{ClO}_4^-$ ) 1000 mg/L -- Dissolve 0.1231 g sodium perchlorate ( $\text{NaClO}_4$ , CASRN [7601-89-0]) in reagent water and dilute to 100 mL in a volumetric flask.

**NOTE:** Stability of standards -- Perchlorate stock standards, stored at room temperature, appear to be very stable and may be stable for an extended period of time. However, specified expiration dates should be marked on each prepared stock standard as part of any laboratory's quality control program. In this regard, it is recommended that stock standards for perchlorate be held for no more than 12 months and an expiration date should be clearly specified on the label.

7.4 Mixed Common Anion Stock Solution - containing the anions chloride, sulfate and carbonate each at 25 mg/mL anion concentration. This solution is used to prepare simulated common anion samples in the determination of the MCT (Section 9.2.8).

7.4.1 Dissolve the following salts in reagent water to a final volume of 25.0 mL:  
1.0 g sodium chloride ( $\text{NaCl}$ , CASRN [7647-14-5]) = 0.61 g  $\text{Cl}^-$   
0.93 g sodium sulfate ( $\text{Na}_2\text{SO}_4$ , CASRN [7757-82-6]) = 0.63 g  $\text{SO}_4^{2-}$   
1.1 g sodium carbonate ( $\text{Na}_2\text{CO}_3$ , CASRN [497-19-8]) = 0.62 g  $\text{CO}_3^{2-}$

## 7.5 Conductivity Meter Calibration Solution

7.5.1 Potassium Chloride (KCl), 745 mg/L (total salt weight) -- Dissolve 0.745 g potassium chloride (KCl, [CASRN 7447-40-7]) in reagent water and dilute to a final volume of 1.00 L in a volumetric flask. On a properly functioning and calibrated conductivity meter, the reference conductance for this solution is 1410 uS/cm at 25 °C.<sup>16</sup>

## 8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

- 8.1 Samples may be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. The volume collected should be sufficient to insure a representative sample, allow for replicate analysis and laboratory fortified matrix analysis, if required, and minimize waste disposal.
- 8.2 Samples do not need to be shipped iced or stored cold in a refrigerator but every effort should be taken to protect the samples from temperature extremes. A thermally insulated sampling kit, designed to fit sampling bottles securely during shipment, should be used to protect the samples from these temperature extremes.
- 8.3 Sample preservation and holding times for the anions are as follows:

<u>Analyte</u>	<u>Preservation</u>	<u>Holding Time</u>
Perchlorate	None required	28 days

**NOTE:** Perchlorate has been shown to be stable for more than 28 days<sup>6</sup> but extended holding time studies (beyond 35 days) were not conducted by EPA. Typically, when analytes are believed to be stable, a 28 day holding time is established as a sufficient time period to permit a laboratory to conduct the analysis.

## 9. QUALITY CONTROL

- 9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The requirements of this program consist of an initial demonstration of laboratory capability, and subsequent analysis in each analysis batch (Section 3.1) of an Instrument Performance Check Standard (IPC), Laboratory Reagent Blank (LRB), Initial Calibration Check Standard (ICCS), Laboratory Fortified Blank (LFB), Continuing and End Calibration Check Standards (CCCS/ECCS), Laboratory Fortified Sample Matrix (LFM) and either a Field, Laboratory or LFM duplicate sample analysis. This section details the specific requirements for each of these QC parameters. The QC criteria discussed in the following sections are summarized in Section 17, Table 5 and

6. The laboratory is required to maintain performance records that define the quality of the data that are generated.

## 9.2 INITIAL DEMONSTRATION OF CAPABILITY

9.2.1 The Initial Demonstration of Capability (IDC) -- This is used to characterize instrument and laboratory performance prior to performing analyses by this method. The QC requirements for the IDC discussed in the following section are summarized in Section 17, Table 5.

9.2.2 Initial demonstration of low system background -- See Section 9.3.1.

9.2.3 Initial Demonstration of Accuracy (IDA) -- Prepare and analyze 7 replicate LFBs fortified at 25.0 ug/L. Calculate the mean measured concentration ( $C_{\bar{x}}$ ) of the replicate values as follows.

$$C_{\bar{x}} = \frac{(C_1 + C_2 + C_3 + \dots + C_n)}{n}$$

where,

$C_{\bar{x}}$  = Mean recovered concentration of the replicate analysis.  
 $C_1, C_2, \dots, C_n$  = Recovered concentrations of the replicate 1, 2, ..., n.  
 $n = 7$

To pass the IDA, the value derived for  $C_{\bar{x}}$  must be within  $\pm 10\%$  of the true value or between 22.5 ug/L and 27.5 ug/L.

9.2.4 Initial Demonstration of Precision (IDP) -- Using the data generated for Section 9.2.3, calculate the percent relative standard deviation (%RSD) of the replicate analysis, as indicated below. To pass the IDP, the %RSD must be less than 10%.

$$\%RSD = \frac{(S_{n-1})}{(C_{\bar{x}})} \times 100$$

where,

$S_{n-1}$  = sample standard deviation (n-1) of the replicate analyses.  
 $C_{\bar{x}}$  = mean recovered concentration of the replicate analysis.

9.2.5 Quality Control Sample (QCS) – After calibration curves have initially been established or have been re-established, or as required to meet data quality needs, verify both the calibration and acceptable instrument performance with the preparation and analyses of an external/second source QCS. If the determined concentrations are not within  $\pm 10\%$  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 IDC or continuing with on-going analyses.

- 9.2.6 Method Detection Limit (MDL) – An MDL must be established using reagent water (blank) fortified at a concentration of three to five times the estimated instrument detection limit.<sup>7,8</sup> To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method over a three day period. These seven MDL replicate analyses may be performed gradually over three days or may represent data that has been collected, at a consistent MDL estimated concentration, over a series of more than three days. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$\text{MDL} = (t) \times (S_{n-1})$$

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<sub>n-1</sub> = sample standard deviation (n-1) of the seven replicate analyses.

- 9.2.6.1 MDLs should be periodically verified, but MUST be initially determined when a new operator begins work or whenever there is a significant change in the background, or instrument response.

**NOTE:** Do not subtract blank values when performing MDL calculations.

- 9.2.7 Minimum Reporting Level (MRL) – The MRL is the threshold concentration of an analyte that a laboratory can expect to accurately quantitate in an unknown sample. The MRL should be established at an analyte concentration either greater than three times the MDL or at a concentration which would yield a response greater than a signal to noise ratio of five. Setting the MRL too low may cause repeated QC failure upon analysis of the ICCS. **Although the lowest calibration standard may be below the MRL, the MRL must never be established at a concentration lower than the lowest calibration standard.**
- 9.2.8 Matrix Conductivity Threshold (MCT) – The MCT is an individual laboratory defined value which must be determined by preparing a series of sequentially increasing, common anion fortified, reagent water samples each contain a constant perchlorate concentration. Initially, a reagent water prepared LFB, containing no common anions, must be analyzed which contains perchlorate at a suggested concentration of 25 ug/L perchlorate. Next, the series of sequentially

increasing anionic solutions are prepared, each containing perchlorate at a suggested concentration of 25 ug/L, which also containing the individual common anions of chloride, sulfate and carbonate, all included at uniform increasing concentrations of 200, 300, 400, 500, 600, 800, and 1000 mg/L for each anion. A concentration of 25 ug/L perchlorate has been suggested assuming the MRL has been set in the range of 3.0 ug/L to 5.0 ug/L. If a laboratory's MRL is higher, choose a perchlorate concentration for this exercise at approximately 5 times that MRL.

- 9.2.8.1 Prepare the mixed common anion stock solution (see Section 7.4) containing chloride, sulfate and carbonate, each at 25 mg/mL.
- 9.2.8.2 Prepare a perchlorate secondary stock dilution standard at 1.00 mg/L from the 1000 mg/L perchlorate stock standard (Section 7.3) by diluting 0.50 mL of the stock solution to a final volume of 500 mL.
- 9.2.8.3 Prepare the LFB at suggested perchlorate concentration of 25 ug/L by diluting 0.625 mL of the perchlorate secondary stock dilution standard (Section 9.2.8.2) to a final volume of 25.0 mL.
- 9.2.8.4 Next, prepare the series of common anion fortified reagent water samples by adding 0.20 mL, 0.30 mL, 0.40 mL, 0.50 mL, 0.60 mL, 0.80 mL, and 1.00 mL of the mixed common anion stock solution (Section 7.4) into separate 25 mL volumetric flasks. Next, add 0.625 mL of the perchlorate secondary stock dilution standard (Section 9.2.8.2) to each 25 mL volumetric flask and dilute to volume with reagent water to yield a final perchlorate concentration of 25.0 ug/L.
- 9.2.8.5 Measure and record the conductance of each of these prepared solutions on a calibrated conductivity meter (This meter must be calibrated as described in Section 10.4 prior to measuring conductance). To use as a relative reference conductance, the 400 mg/L mixed anion sample, which contains chloride at 400 mg/L, sulfate at 400 mg/L and carbonate at 400 mg/L, should display a conductance of between 3200 uS/cm and 3700 uS/cm.
- 9.2.8.6 Analyze each solution, recording the peak area to height (A/H) ratio and the quantified concentration of perchlorate. In many data acquisition and instrument control software, the peak area to height ratio is a definable parameter which can be specified for printout on the analysis report.

- 9.2.8.7 Both the A/H ratio and quantified perchlorate concentration for the LFB and the 200 mg/L mixed common anion solution should be reproducibly consistent but as the common anion levels increase, the A/H ratio will also begin to increase as the peak height is distorted and reduced. As the peak is distorted, the area will also eventually begin to be distorted and the quantitated concentration will be reduced, but this is typically secondary, with the ratio of peak area to height initially predicting this pending quantitation problem.
- 9.2.8.8 Calculate the A/H ratio percent difference ( $PD_{A/H}$ ) between the average A/H ratio for the LFB ( $A/H_{LFB}$ ) and the average A/H ratios for each mixed common anion solutions ( $A/H_{MA}$ ) using the following equation.

$$PD_{A/H} = \frac{*(A/H_{LFB} - A/H_{MA})*}{A/H_{LFB}} \times 100$$

- 9.2.8.9 As the conductivity of the matrices increase, the  $PD_{A/H}$  will increase. The MCT is the matrix conductance where the  $PD_{A/H}$  exceeds 20%. To derive the MCT, perform a linear regression on these data by plotting  $PD_{A/H}$  (as the independent variable, x) versus the matrix conductance (as the dependent variable, y). The resulting regression data should yield an  $r^2$  value of  $> 0.95$ . (See Figure 5) Record the “constant” (intercept value) and the “X-coefficient” (slope) and calculate the MCT as follows,

$$MCT = (20\%) \times (X\text{-coefficient}) + (\text{constant})$$

NOTE: Be careful to consistently apply percentages as either whole numbers or as fractional values ( $20\% = 0.20$ ) for both the regression analysis and the MCT calculation.

- 9.2.8.10 As an alternate to the regression analysis, the laboratory can choose to establish their MCT at the conductance level of the highest mixed anion solution which yielded a  $PD_{A/H}$  value below the 20 % threshold.
- 9.2.8.11 As a final procedure, the laboratory should confirm their perchlorate MRL in a mixed common anion solution which reflects a conductance near (within +/- 10%) that specified as the MCT. This solution must contain perchlorate, at the laboratory determined MRL, as well as the common anions chloride, sulfate and carbonate, prepared consistent with the instruction for the mixed anion solutions in this section and at a concentration estimated to generate a conductance near the MCT.

The conductance of this solution must be measured at within  $\pm 10\%$  of the MCT and following the analysis, the recovered perchlorate must be between 70 - 130% of the MRL concentration. If the MRL recovery fails this criteria, the MCT should be lowered by 10% and this MRL verification must be repeated.

9.2.8.12 Prior to conducting any field sample analysis, the conductivity of that matrix must be determined. When the conductance of a field sample is above the MCT, sample dilution or pretreatment, as described in respective Sections 11.1.3 and 11.1.4 must be performed.

9.3 ASSESSING LABORATORY PERFORMANCE - The following items must be included in every analysis batch (Section 3.1).

9.3.1 Laboratory Reagent Blank (LRB) – An LRB must be prepared and treated exactly as a typical field sample including exposure to all glassware, equipment, solvents, filtration and reagents that are used with field samples. Data produced are used to assess instrument performance of a blank sample and evaluate contamination from the laboratory environment. Values that exceed  $\frac{1}{2}$  the MRL indicate a laboratory or reagent contamination is present. The source of the contamination must be determined prior to conducting any sample analysis. Any sample included in an automated analysis batch which has an invalid LRB, indicated by a quantitated perchlorate that exceeds  $\frac{1}{2}$  the MRL, must be reanalyzed in a subsequent analysis batch after the contamination problem is resolved.

9.3.1.1 When sample matrices have been pretreated to reduce the risk of high common anion interference (Section 11.1.4), a second LRB must be prepared, pretreated in exactly the same manner, and analyzed to confirm no background effects from the pretreatment process are present. If an analysis batch only contains pretreated samples, then only a pretreated LRB is required.

9.3.2 Instrument Performance Check (IPC) -- The MCT, which was determined as part of the IDC in Section 9.2.8, must be verified through the analysis of an IPC. The IPC is three tiered and is used to verify the state of the IC system, over time, to quantitate perchlorate in highly ionic matrices. This must be conducted with each analysis batch since over time, column performance can change.

9.3.2.1 Prepare a mixed common anion solution which reflects a conductance near (within  $\pm 10\%$ ) that specified as the MCT. This solution must be prepared consistent with the instruction in Section 9.2.8, and containing the common anions chloride, sulfate and carbonate as well

1050  
10/10/10

as perchlorate at a suggested concentration of 25 ug/L. This perchlorate concentration has been specified assuming the MRL has been set in the range of 3.0 ug/L to 5.0 ug/L. If a laboratory's MRL is higher, chose a perchlorate concentration for this exercise at approximately 5 times that MRL.

- 9.3.2.2 Confirm the conductance of the IPC and analyze it as the initial sample in the analysis batch. If, after several weeks of storage, the measured conductance of this solution has shifted by more than 10% from the original measured value, prepare a fresh IPC solution. Following the analysis, calculate the  $PD_{A/H}$  (Section 9.2.8.8), by comparing the peak area to height ratio of this IPC mixed anion standard ( $A/H_{MA}$ ) for this analysis batch to the value that was derived for the LFB ( $A/H_{LFB}$ ) either in the original IDC or in the previous analysis batch. As the first tier criteria, the value for  $PD_{A/H}$  must be less than 25% before proceeding with the analysis batch.
- 9.3.2.3 At the second tier criteria, the measured recovery for perchlorate in this IPC must fall between 80% and 120 % (20.0 ug/L to 30.0 ug/L for a 25 ug/L fortification).
- 9.3.2.4 As a third tier and final criteria for the IPC, the laboratory must closely monitor the perchlorate retention time for this analysis. Small variations in retention time can be anticipated when a new solution of eluent is prepared but if sudden shifts of more than 5% are observed in the perchlorate retention time, some type of instrument problem may be present. Potential problems include improperly prepared eluent, erroneous method parameters programmed such as flow rate or some other system problem. The observed retention time for perchlorate should closely replicate the times established when the column was originally installed. As a column ages, it is normal to see a gradual shift and shortening of retention times, but if after several years of use, extensive use over less than a year, or use with harsh samples, this retention time has noticeably shifted to any less than 80% of the original recorded value, the column requires cleaning (according to manufacturer's instructions) or replacement. A laboratory should retain a historic record of retention times for perchlorate to provide evidence of an analytical column's continued performance.
- 9.3.2.5 If any of the conditions defined in Section 9.3.2.2 through 9.3.2.4 are not met, the MCT must be repeated and revised to a more appropriate lower matrix conductivity threshold or the source of the problem must be determined and the IPC reanalyzed.

9.3.3 Laboratory Fortified Blank (LFB) – Prepare a secondary dilution stock using the same stock solution used to prepare the calibration standards. This separate, secondary dilution stock is used as a concentrate to fortify the LFB and the LFM (Section 9.4.1). An external source stock or QCS, which is used to verify the accuracy of the calibration curve when it was initially prepared (Section 10.2.5), should not be used to prepare this secondary dilution stock. Laboratories are required to analyze a LFB (filtered as if it were a field sample) with each analysis batch immediately following the ICCS. The LFB must be prepared with the same solution used to prepare the LFM and should be prepared at concentrations no greater than ten times the highest concentration observed in any field sample and should be varied to reflect the range of concentrations observed in field samples. By analyzing the LFB initially, a control check is performed on the concentrated solution used to prepare the LFM. If any deviations in the perchlorate concentration are present, it will be reflected in the LFB and not exclusively attributed to a matrix upon analysis of the LFM. Calculate accuracy as percent recovery (Section 9.4.1.3). The recovery for perchlorate must fall in the range of 85 - 115% prior to analyzing samples. If the LFB recovery for an analysis batch does not meet these recovery criteria the data are considered invalid, and the source of the problem should be identified and resolved before continuing analyses.

9.3.3.1 When sample matrices have been pretreated to reduce the risk of high common anion interference (Section 11.1.4), a second LFB must be prepared, pretreated in exactly the same manner, and analyzed to confirm no background effects or recovery bias induced by the pretreatment are present. If an analysis batch only contains pretreated samples, then only a pretreated LFB is required.

9.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY - The following must be included in every analysis batch (Section 3.1).

9.4.1 Laboratory Fortified Sample Matrix (LFM) – The laboratory must add a known amount of each target analyte to a minimum of 5% of the collected field samples or at least one with every analysis batch, whichever is greater. Samples which exceed the MCT must either be diluted (Section 11.1.3) or pretreated to reduce the common anion levels (Section 11.1.3). Samples which are pretreated have additional LFM requirements described in Section 11.1.4.6, and must be fortified before pretreatment. For a LFM to be valid, the target analyte concentrations must be greater than the native level and should adhere to the requirement outlined in Section 9.4.1.2. It is recommended that the solutions used to fortify the LFM be prepared from the same stocks used to prepare the calibration standards and not from external source stocks. This will remove the

bias contributed by an externally prepared stock and focus on any potential bias introduced by the field sample matrix.

- 9.4.1.1 The fortified concentration must be equal to or greater than the native sample concentration. Fortified samples that exceed the calibration range must be diluted to be within the linear range. In the event that the fortified level is less than the observed native level of the unfortified matrix, the recovery should not be calculated. This is due to the difficulty in calculating accurate recoveries of the fortified concentration when the native sample concentration to fortified concentration ratio is greater than one.
- 9.4.1.2 For normal drinking waters, the LFM typically should be prepared in the range of 20 - 50 ug/L. The LFM should not be prepared at concentration greater than ten times the highest concentration observed in any field sample and should be varied to reflect the range of concentrations expected in field samples.
- 9.4.1.3 Calculate the percent recovery for each target analyte, corrected for concentrations measured in the unfortified sample. Percent recovery should be calculated using the following equation:

$$\%REC = \frac{(C_s - C)}{s} \times 100$$

where,

%REC = percent recovery,

$C_s$  = measured perchlorate in the fortified sample,

$C$  = measured native perchlorate sample concentration, and

$s$  = concentration equivalent of analyte added to sample.

- 9.4.1.4 Recoveries may exhibit a matrix dependence. If the recovery for perchlorate falls outside 80 - 120%, and the laboratory's performance for all other QC performance criteria is acceptable, the accuracy problem encountered with the fortified sample is judged to be matrix related, not system related. The result for that analyte in the unfortified sample and the LFM must be labeled suspect/matrix to inform the data user that the result is suspect due to matrix effects. Repeated failure to meet suggested recovery criteria indicates potential problems with the procedure and should be investigated.
- 9.4.2 FIELD, LABORATORY DUPLICATES OR DUPLICATE LFM – The laboratory must analyze either a field duplicate, a laboratory duplicate, or a

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duplicate LFM for a minimum of 5% of the collected field samples or at least one with every analysis batch, whichever is greater. The sample matrix selected for this duplicate analysis must contain measurable concentrations of the target anions in order to establish the precision of the analysis set and ensure the quality of the data. Without prior knowledge or strong suspicion that an unknown sample has measurable perchlorate concentrations, the best alternative is to analyze a duplicate LFM.

- 9.4.2.1 Calculate the relative percent difference (RPD) of the initial quantitated concentration ( $I_c$ ) and duplicate quantitated concentration ( $D_c$ ) using the following formula.

$$RPD = \frac{*(I_c - D_c)*}{([I_c + D_c]/2)} \times 100$$

- 9.4.2.2 Duplicate analysis may exhibit a matrix dependence. If the RPD for the duplicate measurements of perchlorate falls outside  $\pm 15\%$  and if all other QC performance criteria are met, laboratory precision is out of control for the sample and perhaps the analytical batch. The result for the sample and duplicate should be labeled as suspect/matrix to inform the data user that the result is suspect due to a potential matrix effect, which led to poor precision. This should not be a chronic problem and if it frequently recurs ( $>20\%$  of duplicate analyses), it indicates a problem with the instrument or individual technique that must be corrected.
- 9.4.3 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options, such as the use of different columns (which meet the criteria in Section 6.1.2.2), injection volumes, 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 and adhere to the condition of conductivity baseline stability found in Section 1.2.1.
- 9.4.4 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. Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant proficiency testing (PT) or performance evaluation (PE) sample studies.

## 10. CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration is required prior to the IDC and before any samples are analyzed, and is required intermittently throughout sample analysis to meet required QC performance criteria outlined in this method and summarized in Table 6. Initial calibration verification is performed using a QCS as well as with each analysis batch using an initial, continuing (when more than 10 field samples are analyzed), and end calibration check standards. The procedures for establishing the initial calibration curve are described in Section 10.2. The procedures to verify the calibration with each analysis batch is described in Section 10.3.

## 10.2 INITIAL CALIBRATION CURVE

10.2.1 Establish ion chromatographic operating parameters equivalent to those indicated in Table 1.

10.2.2 Estimate the Linear Calibration Range (LCR) -- The LCR should cover the expected concentration range of the field samples and should not extend over more than two orders of magnitude in concentration. The restriction of two orders of magnitude is prescribed since beyond this it is difficult to maintain linearity throughout the entire calibration range.

10.2.2.1 If quantification is desired over a larger range, then two separate calibration curves should be prepared.

10.2.2.2 A minimum of three calibration standards are required for a curve that extends over a single order of magnitude and a minimum of five calibration standards are required if the curve covers two orders of magnitude.

10.2.2.3 Since the anticipated concentration range for perchlorate in actual field samples is expected to cover two orders of magnitude, the use of at least five calibration standards in the range 4 - 400  $\mu\text{g/L}$  is recommended.

10.2.3 Prepare the calibration standards by carefully adding measured volumes of the stock standard (Section 7.3) to a volumetric flask and diluting to volume with reagent water.

10.2.4 Inject 1.0 mL of each calibration standard. Tabulate peak area responses against the perchlorate concentration. The results are used to prepare a calibration curve. Acceptable calibration is confirmed after reviewing the curve for linearity (second order fits are also acceptable) and passing the criteria for the initial calibration check standard in Section 10.3.1. Alternately, if the ratio of area to concentration (response factor) is constant over the LCR (indicated by <

15% relative standard deviation), linearity through the origin can be assumed and the average ratio or response factor can be used in place of a calibration curve.

10.2.4.1 Peak areas must be used as a measure of response since they have been found to be more consistent, in terms of quantitation, than peak heights. Peak height can tend to be suppressed as a result of high levels of common anions in a given matrix which can compete for exchange sites leading to peak broadening. Using peak areas, it is the analyst's responsibility to review all chromatograms to insure accurate baseline integration of target analyte peaks, since poorly drawn baselines will significantly influence peak areas.

10.2.5 After establishing or reestablishing calibration curves, the accuracy of this calibration must be verified through the analysis of a QCS or externally prepared second source. The QCS should be prepared at a concentration near the middle of the calibration curve. As specified in Section 9.2.5, determined concentrations must fall within  $\pm 10\%$  of the stated values.

10.3 CONTINUING CALIBRATION VERIFICATION -- Initial calibrations may be stable for extended periods of time. Once the calibration curve has been established it MUST be verified for each analysis batch, prior to conducting any field sample analysis using an Initial Calibration Check Standard. Continuing Calibration Check Standards and End Calibration Check Standards are also required as described in the sections below.

10.3.1 INITIAL CALIBRATION CHECK STANDARD (ICCS) – For each analysis batch the calibration must initially be verified prior to analyzing any samples. The lowest level standard used to prepare the linear calibration curve must be used. In cases where the analyst has chosen to set the MRL above the lowest standard, a standard at a concentration equal to the MRL is acceptable. Percent recovery for the ICCS must be in the range of 75 - 125% before continuing the analysis batch and conducting any sample analyses.

10.3.2 CONTINUING CALIBRATION CHECK/END CALIBRATION CHECK STANDARDS (CCCS/ECCS) -- Continuing calibration check standards MUST be analyzed after every tenth field sample analysis and at the end of the analysis batch as an end calibration check standard. If more than 10 field samples are included in an analysis batch, the analyst must alternate between the middle and high continuing calibration check standard levels.

10.3.2.1 The percent recovery for perchlorate in the CCCS/ECCS must be between 85 - 115%.

10.3.2.2 If during the analysis batch, the measured concentration for perchlorate

in the CCCS or ECCS differs by more than the calibration verification criteria shown above, or if the perchlorate peak retention time shifts outside the retention time window (as defined in Section 11.2.4), all samples analyzed after the last acceptable check standard are considered invalid and must be reanalyzed. The source of the problem must be identified and resolved before reanalyzing the samples or continuing analyses.

10.3.2.3 In the case where the end calibration fails to meet performance criteria, but the initial and middle calibration checks are acceptable, the samples bracketed by the acceptable calibrations may be reported. However, all field samples between the middle and end calibration checks MUST be reanalyzed.

10.4 CONDUCTIVITY METER CALIBRATION -- Prior to conducting the MCT and coinciding with each analysis batch, conductivity meter calibration must be verified or established using a standard KCl solution (Section 7.5).

10.4.1 Thoroughly rinse the conductivity electrode with reagent water. Place the electrode in the reagent water, turn on the meter and confirm the conductance of this blank is  $< 1$  uS/cm.

10.4.2 Pour approximately 15 mL of the standard KCl solution (Section 7.5) into a plastic disposable micro beaker (Section 6.7) and place the electrode into the solution. The reference conductance for this solution is 1410 uS/cm at 25 °C.<sup>16</sup> The conductivity meter must yield a conductance between 1380 uS/cm and 1440 uS/cm to be in calibration.

10.4.3 If the conductivity meter fails calibration, recalibrate the unit per manufacture's instruction and repeat the procedure in 10.4.2 as if the standard solution were an unknown matrix.

## **11. PROCEDURE**

### 11.1 SAMPLE PREPARATION

11.1.1 Samples do not need to be refrigerated but if samples are held refrigerated as a standard practice for sample control, ensure the samples have come to room temperature prior to conducting sample analysis.

11.1.2 MATRIX CONDUCTANCE VERIFICATION - Prior to conducting the analysis of a field sample matrix, the conductance of that matrix must be measured. Matrix conductivity is directly related to the common anion levels

which, at high concentrations, can influence the integrity of the perchlorate analysis.

- 11.1.2.1 Verify conductivity detector calibration by following the procedure outlined in Section 10.4.
  - 11.1.2.2 Pour approximately 15 mL of sample into a plastic disposable micro beaker (Section 6.7) and reseal the sample bottle to protect the sample integrity.
  - 11.1.2.3 Place the electrode into the matrix and measure the conductivity.
  - 11.1.2.4 If the conductance is less than the MCT, continue to Section 11.1.5.
  - 11.1.2.5 If the conductance is greater than the MCT, the matrix requires dilution or pretreatment prior to analysis. The dilution procedure is found in Section 11.1.3. Pretreatment is described in Section 11.1.4.
  - 11.1.2.6 Discard this aliquot of sample and be certain to thoroughly rinse the electrode with reagent water between each matrix conductivity measurement.
- 11.1.3 MATRIX DILUTION - If matrix conductivity is less than the MCT, go to Section 11.1.5.
- 11.1.3.1 A sample can be analyzed once diluted with reagent water to a conductance below the MCT. The exact magnitude of this dilution will adversely increase the MRL by an equivalent proportion.
  - 11.1.3.2 Knowing the matrix conductance exceeds the MCT, estimate the proportion required for the dilution by dividing the measured matrix conductance by the MCT. Round up to the next whole number and dilute the sample by a proportion equivalent to this value. For example, if the established MCT is 6100 uS/cm and a sample reflecting a conductance of 8000 uS/cm was measured, dilute the sample with reagent water by a factor of 2.
  - 11.1.3.3 Measure the conductance of the diluted sample to confirm it is now below the MCT. Analyze the sample as specified in Section 11.1.5 with the understanding that the MRL has now been elevated by a proportion equivalent to the dilution.
  - 11.1.3.4 If perchlorate is measured above the elevated MRL, back calculate



actual field sample concentration and report. If no perchlorate is measured above the elevated MRL and analysis or project objectives required monitoring below the concentration of the elevated MRL, proceed to Section 11.1.4 and pretreat the matrix.

11.1.4 PRETREATMENT FOR MATRICES WHICH EXCEED THE MCT – If matrix conductivity is less than the MCT, go to Section 11.1.5. If sample dilution did not yield the required results, sample pretreatment should be employed. When the MCT is exceeded, it is most often due to a high levels of common anions (chloride, sulfate, and carbonate) in a particular matrix. If the analyst were to attempt the IC analysis of this particular matrix, the common anions present in the sample would distort the baseline and negatively affect the accurate quantitation of perchlorate. To effectively reduce a significant amount of these anions which contribute to the high conductivity reading, a series of pretreatment cartridges must be employed. For this pretreatment, three cartridges are attached in series in the following order: Ba, Ag, and H. It is recommended that all three cartridges be employed unless the analyst has specific knowledge that a matrix primarily has high levels of a specific common anion.

11.1.4.1 Individually and thoroughly rinse each pretreatment cartridge with reagent water in order to insure all residual background contaminants are removed from the cartridge. Perform this rinse per manufacturer's instructions.

11.1.4.2 Prior to pretreating any field samples, prepare and pretreat both an LRB and an LFB. These pretreated quality control samples are required when an analysis batch contains a matrix which must be pretreated. This pretreatment is conducted by placing the cartridges in the following prescribed series (-->Ba-->Ag-->H). The pretreated LRB and LFB are used to verify that no background interference or bias is contributed by the pretreatment. If a response is observed in the pretreated LRB, triple or quadruple the volume of reagent water rinse suggested by the manufacturer in Section 11.1.4.1 and repeat until a blank measures no more than ½ the MRL. If this additional rinsing procedure is required, it must be consistently applied to all the cartridges prior to conducting any matrix pretreatment.

11.1.4.3 Filter 3 mL of sample through the series of rinsed, stacked cartridges as an initial sample rinse (Ba, Ag and H) at a flow rate of 1.0 mL/ min or less (approximately one drop every 3 to 4 seconds). This flow rate is critical to the pretreatment and must be carefully followed. Discard this fraction and begin collecting the pretreated sample aliquot of

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collected sample.

- 11.1.4.4 When sufficient volume has been collected, measure the conductance of the pretreated sample aliquot being certain the conductivity meter's probe has been thoroughly rinsed and excess water has been shaken from the tip. If the conductance is now below the MCT, the sample is ready for analysis. If the conductance is still above the MCT, the flow rate through the pretreatment cartridge is likely too fast and the pretreatment should be repeated with new cartridges. In some instances, double pretreatment cartridges may need to be applied. When this pretreatment is performed properly, U.S.EPA has found 70% to 95% reduction in matrix conductance with good recoveries for perchlorate.
- 11.1.4.5 Place this aliquot of pretreated sample into an autosampler vial as described in Section 11.1.3.
- 11.1.4.6 In order to ensure data quality, all samples which fail the MCT and have been selected for pretreatment, as described in Section 11.1.4, must also be used to prepare an LFM. This LFM must be fortified with perchlorate at concentrations close to, but greater than, the level determined in the native sample prior to the pretreatment. Initially, the pretreated sample is analyzed and perchlorate level is determined. Then, a second aliquot of sample must be fortified with perchlorate, pretreated to reduce the high common anion levels, and analyzed to assess perchlorate recovery from that matrix. This additional QC is required to rule out matrix effects and to confirm that the laboratory performed the pretreatment step appropriately. **If the perchlorate recovery falls outside the acceptance range of 80 - 120% (Section 9.4.1.4), that particular sample should be reported as suspect/matrix.**
- 11.1.4.7 The pretreatments prescribed above are effective at reducing the chloride and sulfate content of a sample matrix but will not reduce matrix concentrations of other anions such as nitrate or phosphate.
- 11.1.5 Pour approximately 15 mL of sample into a micro beaker (Section 6.7) and reseal the sample bottle to protect the sample integrity. Using a Luer lock, plastic 10 mL syringe, withdraw approximately 10 mL of sample from the micro beaker and attach a 0.45  $\mu\text{m}$  particulate filter (Section 6.11), which has been demonstrated to be free of ionic contaminants, directly to the syringe. Filter the sample into an autosampler vial or manually load the injection loop injecting a fixed amount of filtered, well mixed sample. If using a manually

loaded injection loop, flush the loop thoroughly between sample analysis using sufficient volumes of each new sample matrix.

11.1.5.1 If the autosampler vials or vial caps are designed to automatically filter the sample matrix as the sample is loaded on the IC system, this filtration procedure can be omitted and the sample can be directly transferred to the autosampler vial.

## 11.2 SAMPLE ANALYSIS

- 11.2.1 Table 1 summarizes the recommended operating conditions for the ion chromatograph. Included in this table is the estimated retention time for perchlorate which has been achieved by this method. Other columns, chromatographic conditions or detectors may be used if the requirements of Sections 1.2.1, 6.1.2.2 and 9.2 are met.
- 11.2.2 Establish a valid initial calibration and verify this calibration by conducting a QCS as described in Section 10.2 and complete the IDC (Section 9.2). Initially, analyze the IPC solution, followed by the LRB. Then confirm the IC system calibration by analyzing an ICCS (Section 10.3.1) and, if required, recalibrate as described in Section 10.2. Lastly, analyze the LFB.
- 11.2.3 Inject 1.0 mL of each filtered sample. Use the same size loop for standards and samples. An automated constant volume injection system may also be used. Record the resulting peak size in area units and retention time for each analyte.
- 11.2.4 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards measured over several days. Three times the standard deviation of retention time may be used as a suggested window size but the retention time window should not extend beyond  $\pm 5\%$  of the retention time for perchlorate. The experience of the analyst should weigh heavily in the interpretation of these chromatograms.
- 11.2.5 If the response of a sample analyte exceeds the calibration range, the sample must be diluted with an appropriate amount of reagent water and reanalyzed. If this is not possible then three new calibration concentrations must be employed to create a separate high concentration calibration curve, one standard near the estimated concentration and the other two bracketing around an interval equivalent to approximately  $\pm 25\%$  the estimated concentration. The response generated by these three new high concentration calibration standards must not exceed the upper linear range for the conductivity detector. The latter procedure

involves significantly more time than a simple sample dilution therefore, it is advisable to collect sufficient sample to allow for sample dilution and sample reanalysis, if required.

11.2.6 Should more complete resolution be needed between perchlorate and a coeluting, shoulder peak, the eluent (Section 7.2) may be diluted. This will spread out the peaks, causing later elution of perchlorate. Analysts are advised to carefully evaluate any of these eluent dilutions since when these eluent changes are incorporated, other coelutions may be encountered which were not initially evident. Additionally, the analyst must verify that this dilution does not negatively affect performance by repeating and passing all the QC criteria in Section 9, and by reestablishing a valid initial calibration curve (Section 10.2).

11.2.6.1 Eluent dilution will reduce the overall response of an anion due to chromatographic band broadening which will be evident by shortened and broadened peaks. This will adversely effect the MDLs for each analyte.

### 11.3 AUTOMATED ANALYSIS WITH METHOD 314.0

11.3.1 Laboratories conducting analyses on large numbers of samples often prepare large analysis batches that are run in an automated manner. When conducting automated analyses, careful attention must be paid to ensure sufficient volume of eluent in the reservoir is available to sustain extended operation. In order to ensure their data are of acceptable quality, laboratories must ensure that all QC performance criteria are met throughout the analysis batch through subsequent careful inspection of the data.

11.3.2 Analysis sequences must be carefully constructed to meet required QC specifications and frequency (Table 6). To help with this task, an acceptable sequence for a sample analysis batch, with all the method-required QC, is shown in Table 7. This schedule is included only as an example of a hypothetical analysis batch which contains normal sample matrices as well as samples which have failed the MCT. Within this analysis batch, references to exact concentrations for the ICCS, CCCS and ECCS are for illustrative purposes only.

11.3.3 Table 7 may be used as a guide when preparing analysis batches. Additional batches may be added sequentially on to the end of these types of schedules as long as all QC samples, which define an individual batch (IPC, LRB, ICCS, LFB, LFM, etc.) are individually reanalyzed with each successive serial batch and the QC criteria for these analyses are continually met (from the IPC through ECCS).

## **12. DATA ANALYSIS AND CALCULATIONS**

- 12.1 Identify perchlorate in the sample chromatogram by comparing the retention time of a suspect peak within the retention time window to the actual retention time of a known analyte peak in a calibration standard. If the perchlorate retention time has slightly shifted (generally towards shorter times) since the initial calibration, but is still within acceptance criteria and are reproducible during the analysis batch, the analyst should use the retention time in the daily calibration check standards to confirm the presence or absence of perchlorate anion.
  - 12.1.1 If a low concentration of perchlorate is suspected in an unknown sample, but the retention time has drifted to the edge of the retention time window, a low level perchlorate LFM, prepared at nearly the same concentration as the suspect peak, should be prepared from this sample matrix to confirm the matrix induced retention time shift. If the fortified sample reveals a split or shouldering peak response, the low concentration in the unfortified sample is likely an interferant and should not be reported as perchlorate.
- 12.2 Compute sample concentration using the initial calibration curve generated in Section 10.2.
- 12.3 Report ONLY those values that fall between the MRL and the highest calibration standards. Samples with a perchlorate response which exceeds the highest calibration standard concentration must be diluted and reanalyzed. When this is not possible the alternate calibration procedures described in Section 11.2.5 must be followed. Samples with perchlorate identified but quantitated below the concentration established by the lowest calibration standard, may be reported as “trace present” above the MDL but below the minimum reporting limit (MRL) and therefore not reported as a quantitated concentration.
- 12.4 Report results in  $\mu\text{g/L}$ .

## **13. METHODS PERFORMANCE**

- 13.1 Table 1 gives the standard conditions, typical retention time, single laboratory MCT and single laboratory MDL in reagent water, as determined for perchlorate. This retention time is graphically indicated in the chromatograms in Figures 1 through 4.
- 13.2 Table 2 shows the precision and accuracy of the perchlorate measurement at two fortified concentrations, in reagent water, simulated high ionic strength water (HIW), simulated high organic content water (HOW), ground water, untreated surface water and treated surface water. The mean perchlorate recovered concentration (accuracy relative to the fortified level) and the precision (expressed as %RSD of the replicate analysis) are tabulated. The HIW was designed to simulate a high ionic strength field

sample and the HOW designed to simulate a high organic content field sample. The HIW was prepared from reagent water which was fortified with the common anions of chloride at 400 mg/L, carbonate at 600 mg/L, and sulfate at 500 mg/L. The HOW was prepared from reagent water fortified with 10.0 mg/L fulvic acid.

- 13.3 Table 3 shows the stability data for perchlorate held for 35 days and stored under various conditions. Conditions investigated included sample bottle construction (HDPE plastic vs. glass), storage condition (refrigerated vs. held at room temperature) and various matrices including some with a measured perchlorate concentration assumed to contain microbiological constituents acclimated to the presence of the anion. Matrices without perchlorate were fortified at 25 ug/L. Each data point in this table represents the mean percent recovery following triplicate analyses. These data were used to formulate the holding times shown in Section 8.3.
- 13.4 Table 4, in conjunction with the chromatograms overlaid in Figure 4 as well as the linear regression plots in Figure 5, show the results of the single laboratory MCT determination. The data presented in Table 4 and graphically illustrated in Figure 5, show results for not only the AS16 but also the AS11 and AS5. The chromatogram shown in Figure 4 were generated using the AS16 column.

#### **14. 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 chemicals purchased should be based on expected usage during its shelf-life and the 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. 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. REFERENCES

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**17. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA**

**TABLE 1. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS IN REAGENT WATER FOR PERCHLORATE.**

**Standard Conditions and Equipment<sup>(a)</sup>:**

Ion Chromatograph:	Dionex DX500
Sample Loop:	1000 µL
Eluent:	50 mM NaOH
Eluent Flow:	1.5 mL/min
Columns :	Dionex AG16, 4 mm / AS16, 4 mm
Typical System Backpressure:	2600 psi
Suppressor:	ASRS ULTRA (P/N 53946), external water mode, 300 mA current
Detectors:	Suppressed Conductivity Detector, Dionex CD20
	Background Conductivity: 2 - 3 µS

Determined MCT<sup>(b)</sup>: 6100 uS/cm

Recommended method total analysis time: 15 minutes (may be shortened to 12 minutes)

**Analyte Retention Times and Method Detection Limits (MDLs):**

Analyte	Retention Time <sup>(c)</sup> (min.)	MDL DETERMINATION		
		Fortified Conc. (µg/L)	# of Reps.	MDL (µg/L)
Perchlorate	10.1 ± 0.2	2.0	7	0.53

- (a) Mention of trade names or commercial products does not necessarily constitute endorsement or recommendation for use.
- (b) This was the single laboratory MCT determined for these conditions listed (See Table 4 and Figure 5 for more detail as well as data pertaining to the AS11 and AS5).
- (c) Reference to chromatograms in Figure 1 through 4.

**TABLE 2. SINGLE LABORATORY PRECISION AND RECOVERY FOR PERCHLORATE IN VARIOUS MATRICES**

Matrix	Matrix Conductivity uS/cm	Unfortified Conc. (µg/L)	Fortified Conc. (µg/L)	# of Reps.	Mean (µg/L)	Mean %REC	SD(n-1)	%RSD
Reagent Water	~ 1	<MRL <sup>(a)</sup>	4.00	8	4.04	101%	0.43	10.6%
			25.0	8	26.2	105%	0.89	3.4%
Synthetic High Inorganic Water <sup>(b)</sup>	4200	<MRL	4.00	8	3.42	86%	0.27	7.9%
			25.0	8	24.1	96%	0.46	1.9%
Synthetic High Organic Water <sup>(c)</sup>	5.0	<MRL	4.00	8	3.84	96%	0.38	10.0%
			25.0	8	25.7	103%	1.12	4.4%
Ground Water (high TDS)	710	<MRL	4.00	8	4.22	106%	0.54	12.8%
			25.0	8	26.5	106%	0.62	2.3%
Untreated Surface Water	460	<MRL	4.00	8	4.46	112%	0.24	5.4%
			25.0	8	28.3	113%	0.29	1.0%
Chlorinated Surface Water	460	<MRL	4.00	8	4.18	105%	0.23	5.6%
			25.0	8	28.0	112%	0.63	2.3%

(a) <MRL = analyte was not detected above the laboratory minimum reporting level (MRL) of 4.0 µg/L.

(b) Synthetic High Inorganic Water was prepared from reagent water and contained synthetic high TDS or common anion levels of 400 mg/L chloride, 500 mg/L sulfate and 600 mg/L carbonate.

(c) Synthetic High Organic Water contained 10 mg/L fulvic acid (extracted and crystallized from untreated surface water) fortified into reagent water.

Note: These data were collected using the equipment and conditions listed in Table 1.

**TABLE 3. STABILITY STUDY RESULTS FOR PERCHLORATE IN VARIOUS MATRICES****A. Stability when stored in various sampling bottles - All stored at room temperature**

Matrix	Bottle type	Unfortified Conc.(µg/L)	Fortified Conc.(µg/L)	Analyte % Recovery				
				Day 0	Day 7	Day 14	Day 28	Day 35
Reagent Water	Clear Glass	<MRL <sup>(a)</sup>	25.0	108%	101%	88%	91%	109%
Reagent Water	Amber Glass	<MRL	25.0	108%	101%	91%	90%	107%
Reagent Water	Opaque HDPE Plastic	<MRL	25.0	108%	97%	92%	89%	107%
Reagent Water	Translucent HDPE Plastic	<MRL	25.0	108%	105%	93%	90%	108%

**B. Stability in various matrices under different storage conditions -**

All samples stored in HDPE, opaque sampling bottles and fortified with 25.0 µg/L perchlorate.

Matrix	Storage Condition	Unfortified Conc.(µg/L)	Matrix Cond.uS/cm	Analyte % Recovery				
				Day 0	Day 7	Day 14	Day 28	Day 35
Reagent Water	Room Temp.	<MRL	< 1	104%	104%	95%	87%	107%
	Refrigerated	<MRL		104%	102%	94%	88%	107%
Treated Surface Water #1	Room Temp.	<MRL	520	109%	105%	101%	99%	111%
	Refrigerated	<MRL		109%	102%	100%	97%	108%
Treated Surface Water #2	Room Temp.	<MRL	510	107%	115%	102%	99%	113%
	Refrigerated	<MRL		107%	113%	103%	99%	111%
Untreated Surface Water #1	Room Temp.	<MRL	470	110%	115%	110%	106%	110%
	Refrigerated	<MRL		110%	114%	110%	105%	111%
Untreated Surface Water #2	Room Temp.	<MRL	700	105%	112%	110%	104%	107%
	Refrigerated	<MRL		105%	112%	111%	103%	107%
Untreated Surface Water #3	Room Temp.	<MRL	920	109%	109%	113%	104%	110%
	Refrigerated	<MRL		109%	105%	111%	103%	105%
Untreated Surface Water #4	Room Temp.	<MRL	930	107%	105%	110%	106%	105%
	Refrigerated	<MRL		107%	106%	107%	105%	106%
Ground Water #1	Room Temp.	<MRL	1900	110%	113%	103%	101%	107%
	Refrigerated	<MRL		110%	112%	105%	103%	107%

**C. Stability of native perchlorate in matrices stored under different storage conditions -**

All samples stored in HDPE, opaque sampling bottles.

Matrix	Storage Condition	Matrix Cond. uS/cm	Measured concentration, µg/L				
			Day 0	Day 7	Day 14	Day 28	Day 35
Ground Water #2 (with native ClO <sub>4</sub> <sup>-</sup> )	Room Temp.	603	1090	1110	1080	990	1100
	Refrigerated		1090	1110	1080	1010	1110
Ground Water #3 (with native ClO <sub>4</sub> <sup>-</sup> )	Room Temp.	960	1010	1040	1010	950	1000
	Refrigerated		1010	1040	1020	940	1030
Ground Water #4 (with native ClO <sub>4</sub> <sup>-</sup> )	Room Temp.	750	439	450	427	407	434
	Refrigerated		439	441	427	400	434

(a) &lt;MRL = analyte was not detected above the laboratory minimum reporting level (MRL) of 4.0 µg/L.

Note: Each data point represented the average from triplicate analysis.

**TABLE 4. SINGLE LABORATORY RESULTS FOR THE DETERMINATION OF MCT - Determination on the AS16, AS11 and the AS5.**

<b>AS16 Studies - Perchlorate fortified at 25 ug/L</b>								
Sample	Conductivity uS/cm	RT min.	Measured ClO <sub>4</sub> <sup>-</sup> , ug/L	%Rec	Area	Height	A/H ratio	PD <sub>A/H</sub>
LFB	< 1	10.3	25.3	101%	20268	1151	17.6	0.00%
MA(50) <sup>(a)</sup>	540	10.3	26.0	104%	20799	1135	18.3	4.07%
MA(100)	932	10.3	26.3	105%	21060	1144	18.4	4.54%
MA(200)	1770	10.2	26.2	105%	20998	1112	18.9	7.24%
MA(400)	3570	10.2	25.2	101%	20170	1028	19.6	11.4%
MA(600)	5010 <sup>(b)</sup>	10.2	24.2	97%	19307	954	20.2	14.9%
MA(800)	6450	10.1	25.1	100%	20038	932	21.5	22.1%
MA(1000)	7820	10.2	24.3	97%	19400	878	22.1	25.5%

<b>AS11<sup>(c)</sup> Studies - Perchlorate fortified at 25 ug/L</b>								
Sample	Conductivity uS/cm	RT min.	Measured ClO <sub>4</sub> <sup>-</sup> , ug/L	%Rec	Area	Height	A/H ratio	PD <sub>A/H</sub>
LFB	< 1	8.9	25.0	100%	25213	1591	15.8	0.00%
MA(50) <sup>(a)</sup>	540	8.9	25.2	101%	25445	1515	16.8	5.98%
MA(100)	932	9.0	25.0	100%	25192	1486	17.0	6.98%
MA(200)	1770 <sup>(b)</sup>	9.0	24.1	96%	24340	1384	17.6	11.0%
MA(400)	3570	9.0	23.6	94%	23855	1243	19.2	21.1%
MA(600)	5010	9.0	22.7	91%	22922	1101	20.8	31.4%
MA(800)	6450	8.9	19.9	80%	20243	870	23.3	46.8%
MA(1000)	7820	8.8	17.0	68%	17407	678	25.7	62.0%

<b>AS5<sup>(d)</sup> Studies - Perchlorate fortified at 25 ug/L</b>								
Sample	Conductivity uS/cm	RT min.	Measured ClO <sub>4</sub> <sup>-</sup> , ug/L	%Rec	Area	Height	A/H ratio	PD <sub>A/H</sub>
LFB	< 1	9.7	22.75	91.0%	30348	1780	17.0	0.00%
MA(50) <sup>(a)</sup>	540	9.7	24.89	99.6%	33505	1751	19.1	12.2%
MA(100)	932	9.7	23.72	94.9%	31776	1721	18.5	8.30%
MA(200)	1770 <sup>(b)</sup>	9.7	22.99	92.0%	30704	1591	19.3	13.2%
MA(400)	3570	9.6	23.51	94.0%	31474	1478	21.3	24.9%
MA(600)	5010	9.6	23.84	95.4%	31948	1441	22.2	30.0%
MA(800)	6450	9.6	21.01	84.0%	27792	1214	22.9	34.3%
MA(1000)	7820	9.6	22.95	91.8%	30650	1183	25.9	52.0%

- (a) "MA" indicates mixed common anion solution with each anion (chloride, sulfate and carbonate) included in the sample matrix at the parenthetical mg/L concentration for each anion.
- (b) If the regression analysis is not performed on these data, 5010 uS/cm, 1770 uS/cm and 1770 uS/cm would be the default MCT for the AS16, AS11 and AS5, respectively, as described in Section 9.2.8.10. See Figure 5 for a graphical representation of this data, applying a regression analysis of PD<sub>A/H</sub> vs matrix conductivity for the AS16, AS11 and AS5.
- (c) AS11 conditions: See reference #2 and #3.
- (d) AS5 conditions: See reference #1.

**TABLE 5. INITIAL DEMONSTRATION OF CAPABILITY QC REQUIREMENTS.**  
**Requirements prior to beginning any analysis batch**

Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 9.2.2 9.3.1	Initial Demonstration of Low System Background	Analyze a method blank (LRB) and determine that all target analytes are below ½ of the proposed MRL prior to performing the IDC.	The LRB concentration must be ≤½ of the proposed MRL.
Sect. 9.2.3	Initial Demonstration of Accuracy (IDA)	Analyze 7 replicate LFBs fortified with perchlorate at 25 ug/L. Calculate the mean recovered concentration ( $C_x$ ) See Equation in Section 9.2.3.	The $C_x$ must be ± 10% of true value.
Sect. 9.2.4	Initial Demonstration of Precision (IDP)	Calculate percent relative standard deviation (%RSD) of IDA replicates. See Equation in Section 9.2.4.	The %RSD must be ≤10%
Sect. 9.2.5	Quality Control Sample (QCS)	Initially, upon reestablishing calibration or at least quarterly analyze a QCS from an external/second source.	The QCS must be ± 10% of the true value.
Sect. 9.2.6	Method Detection Limit (MDL) Determination	Select a fortifying level at 3-5 times the estimated instrument detection limit. Analyze 7 replicate LFBs over multiple days and calculate MDL using equation in Section 9.2.6 - do not subtract blank	
Sect. 9.2.7	Minimum Reporting Level (MRL)	An MRL should be established for perchlorate during the IDC.	The low CAL standard can be lower than the MRL, but the MRL MUST be no lower than the low CAL standard
Sect. 9.2.8	Matrix Conductivity Threshold (MCT)	Prepare a series of LFB samples, each containing a suggested perchlorate concentration of 25 ug/L, at sequentially increasing fortified levels of common anions. Measure sample conductance and analyze each, calculate average A/H ratios and $PD_{A/H}$ (using equation in Section 9.2.8.8). Perform linear regression to calculate MCT (using equation in Section 9.2.8.9) or follow step outlined in Section 9.2.8.10.	MCT, based upon linear regression, is point where $PD_{A/H}$ equals 20%.  Alternatively, the MCT is set at the highest measured conductance observed in the last fortified MCT sample to yield a $PD_{A/H}$ value below 20%.
Sect. 9.2.8.11	MRL verification	Verify the MRL in a solution prepared at the MCT.	Prepared within ±10% of the MCT. Perchlorate recovery must be 70- 130% of the MRL.

**TABLE 6. QUALITY CONTROL REQUIREMENTS (SUMMARY).**

**Requirements specific for each analysis batch**

Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 8.3	Sample Holding Time / Preservation / Storage	Perchlorate 28 days No Preservation technique required. Room Temperature adequate for shipping and storage.	Holding time must not be exceeded.
Sect. 10.2	Initial Calibration	Generate calibration curve. At least 5 calibration standards are recommended.	MRL MUST be no lower than the lowest calibration standard
Sect. 9.3.2	Instrument Performance Check (IPC)	Designed to verify Matrix Conductivity Threshold (MCT). Prepare mixed common anion solution at the MCT (prepared consistent with procedures in Section 9.2.8). Confirm the sample's conductance and analyze at the beginning of each analysis batch.	Prepared within $\pm 10\%$ of the MCT.  IPC solution conductance verified to within $\pm 10\%$ of original measured value (when originally prepared)  $PD_{A/H}$ (when compared to the $A/H_{LFB}$ ) must be $< 25\%$ .  Perchlorate quantitated between 80 - 120% of fortified level.  $< 5\%$ shift in perchlorate retention time.
Sect. 10.3.1	Initial Calibration Check (ICCS)	With each analysis batch, initially verify calibration at the MRL by analyzing an initial low-level continuing calibration check standard (ICCS).	Recovery must be 75-125% of the true value.
Sect. 10.3.2	Continuing Calibration (CCCS) and End Calibration Checks (ECCS)	Alternately analyze separate mid and high level CCCS/ECCS after every 10 samples and after the last sample in an analysis batch.	Recoveries must fall between 85 - 115%
Sect. 9.3.1	Laboratory Reagent Blank (LRB)	Include LRB with every analysis batch (up to 20 samples) Analyze prior to analyzing field samples	Perchlorate must be $\leq \frac{1}{2}$ MRL
Sect. 9.3.1.1	PRETREATED Laboratory Reagent Blank (LRB)	REQUIRED in any analysis batch which includes samples which have exceeded the MCT and have been pretreated in any way to reduce the common anion levels.	Perchlorate must be $\leq \frac{1}{2}$ MRL

**TABLE 6. QUALITY CONTROL REQUIREMENTS (SUMMARY CONTINUED).**  
**Requirements specific for each analysis batch**

Reference	Requirement	Specification and Frequency	Acceptance Criteria
Sect. 9.3.3	Laboratory Fortified Blank (LFB)	Laboratory must analyze LFB in each analysis batch following the ICCS. Calculate %REC prior to analyzing samples. The concentration selected for the LFB in subsequent analysis batches should be varied throughout the calibration range.	Recovery for LFB MUST be 85 - 115% prior to analyzing samples. Sample results from batches that fail LFB are invalid.
Sect. 9.3.3.1	PRETREATED Laboratory Fortified Blank (LFB)	REQUIRED in any analysis batch which includes samples which have exceeded the MCT and have been pretreated in any way to reduce the common anion levels. Fortification must be made prior to pretreatment	Recovery for pretreated LFB MUST be 85 - 115% prior to analyzing samples. Sample results from batches that fail a pretreated LFB are invalid.
Sect. 9.4.1	Laboratory Fortified Sample Matrix (LFM)	Must add known amount of perchlorate to a minimum of 5% of field samples or at least one within each analysis batch.  LFM must be fortified above the native level and at no greater than 10 x the highest field sample concentration. Calculate target analyte recovery using formula (Sect. 9.4.1.3).	Recovery must be 80 - 120%  If fortified sample fails the recovery criteria, label both as suspect/matrix.
Sect. 11.1.4.6	SPECIAL LFM for matrices requiring pretreatment	When a sample exceeds the MCT and pretreatment is employed to reduce the common anion levels, an additional LFM must be prepared from this matrix and subsequently pretreated exactly as the unfortified matrix.	Same criteria, recoveries must be 80 -120%.
Sect. 9.4.2	Field or Laboratory Duplicates or LFM Duplicate	Analyze either a field, laboratory or LFM duplicate for a minimum of 5% of field samples or at least one within each analysis batch. Calculate the relative percent difference (RPD) using formula in Section 9.4.2.1.	RPD must be $\pm 15\%$ .
Sect. 6.1.2.2	ALTERNATE IC analytical column performance criteria	If a laboratory chooses an alternate analytical column for this analysis, it must be hydrophilic and pass the criteria for Peak Gaussian Factor (PGF) using equation (Sect. 6.1.2.2).	PGF must fall between 0.80 and 1.15.

**TABLE 7. EXAMPLE SAMPLE ANALYSIS BATCH WITH QUALITY CONTROL REQUIREMENTS**

<b>Injection #</b>	<b>Sample Description</b>	<b>Acceptance Criteria</b>
1	Instrument Performance Check Standard at MCT	PD <sub>A/H</sub> for IPC < 25%
2	Laboratory Reagent Blank (LRB)	≤ ½ MRL
3	ICCS at the MRL (4.0 µg/L)	3.00 to 5.00 µg/L
4	Laboratory Fortified Blank (LFB)	Recovery of 85 - 115%
5	Sample 1	normal analysis
6	Sample 1 - Laboratory Duplicate (LD) <sup>(a)</sup>	± 15 % RPD
7	Sample 2	normal analysis
8	Sample 2 - Laboratory Fortified Matrix (LFM) <sup>(a)</sup>	Recovery of 80 - 120%
9	Sample 3	normal analysis
10	Sample 4	normal analysis
11	Sample 5	normal analysis
12	Sample 6	normal analysis
13	Sample 7	normal analysis
14	Sample 8	normal analysis
15	Sample 9	normal analysis
16	Sample 10	normal analysis
17	CCCS (25.0 ug/L)	21.3 to 28.8 ug/L
18	Sample 11 (failed MCT, matrix conductance = 8000 uS/cm) - Analyzed diluted (Section 11.1.3) by factor of 2 or by 50% with reagent water (diluted matrix conductance = 3800 uS/cm).	MRL increases from 4 to 8 ug/L, noted in analysis report - sample found to contain 50 ug/L (measured at 25 ug/L in diluted sample)
19	Sample 12	normal analysis
20	Sample 13	normal analysis
<b>CONTINUED TO NEXT PAGE</b>		

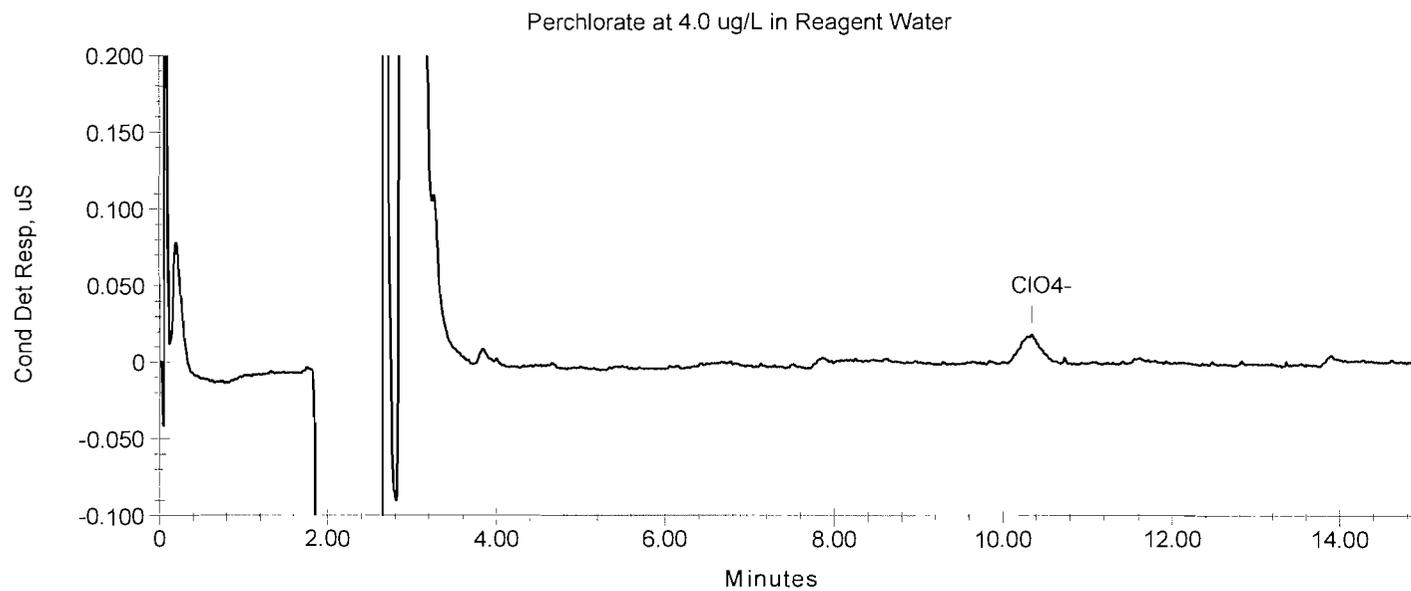
Injection #	Sample Description	Acceptance Criteria
21	Sample 14 (failed MCT, matrix conductance=15000 uS/cm) Analyzed diluted (Section 11.1.3) by a factor of 3 or by 33% with reagent water (Diluted matrix conductance = 4600 uS/cm)	MRL increases from 4 to 12 ug/L, noted in analysis report - No perchlorate > 12ug/L measured - project required monitoring to MRL - sample pretreatment is therefore required
22	Ba/Ag/H Pretreated LRB (Section 9.3.1.1)	≤ ½ MRL
23	Ba/Ag/H Pretreated LFB (Section 9.3.3.1)	Recovery of 85 - 115%
24	Sample 14 - Ba/Ag/H pretreated (Section 11.1.4), following pretreatment the matrix conductance = 230 uS/cm.	normal pretreated analysis perchlorate < MRL of 4.0 ug/L
25	Sample 14 <sup>(b)</sup> - pretreated LFM (Section 11.1.4.6)	Recovery of 80 - 120%
26	Sample 15	normal analysis
27	Sample 16	normal analysis
28	Sample 17	normal analysis
29	Sample 18	normal analysis
30	Sample 19 <sup>(b)</sup>	normal analysis
31	ECCS (100 µg/L)	85.0 to 125 µg/L

<sup>(a)</sup> If no analytes are observed above the MRL for a sample, an alternate sample which contains reportable values should be selected as the laboratory duplicate. Alternately, the LFM can be selected and reanalyzed as the laboratory duplicate ensuring the collection of QC data for precision.

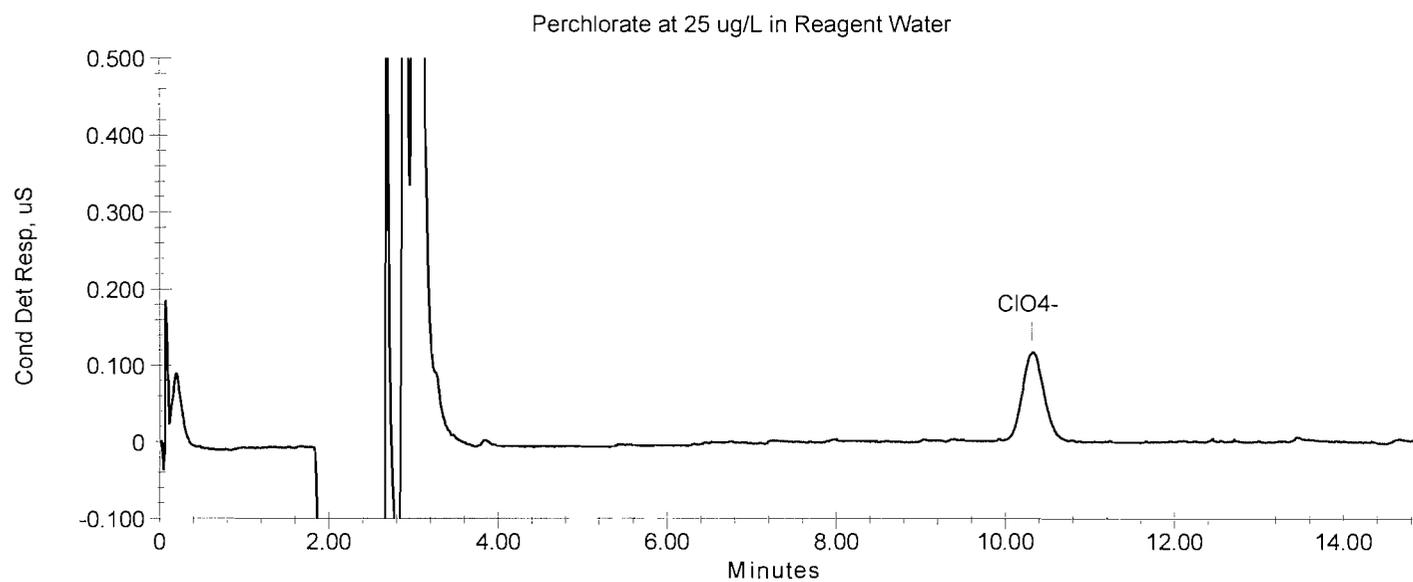
<sup>(b)</sup> Sample #19 (inj #30) was the final field sample permitted in this batch but 20 total field samples were analyzed. Sample #14 (inj #21 and #24) was analyzed both initially as a diluted sample and subsequently as a pretreated sample, therefore it accounted for two “field sample analyses” toward the maximum of twenty in an analysis batch (Section 3.1).

Note: Sample #11 and #14 illustrate examples of proper ways to handle sample matrices which exceed the MCT.

**FIGURE 1. CHROMATOGRAM OF LOW LEVEL PERCHLORATE (4.0 ug/L) IN REAGENT WATER (Conditions as indicated in Table 1)**

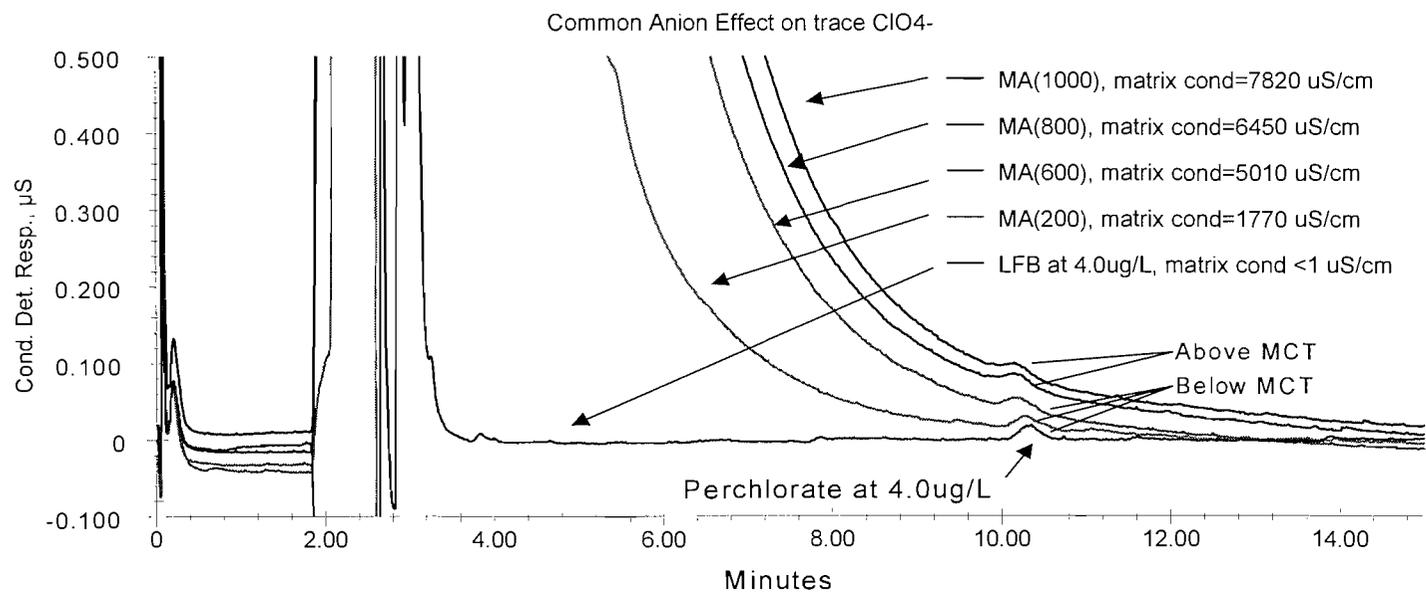


**FIGURE 2. CHROMATOGRAM OF 25 ug/L PERCHLORATE IN REAGENT WATER  
(Conditions as indicated in Table 1)**

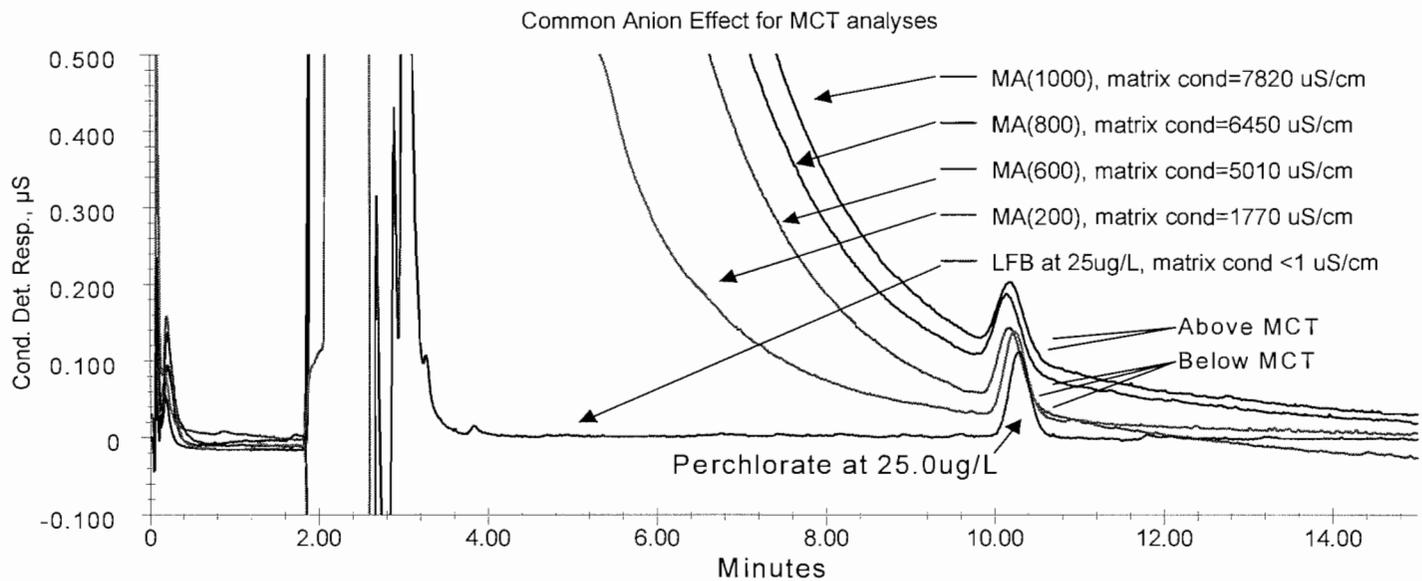


ADFC  
Hazardous Waste  
Division

**FIGURE 3. STACKED CHROMATOGRAMS INDICATING INFLUENCE OF HIGH CONCENTRATIONS OF COMMON ANIONS ON LOW CONCENTRATION MEASUREMENT OF PERCHLORATE AT 4.0 ug/L (Conditions as indicated in Table 1)**

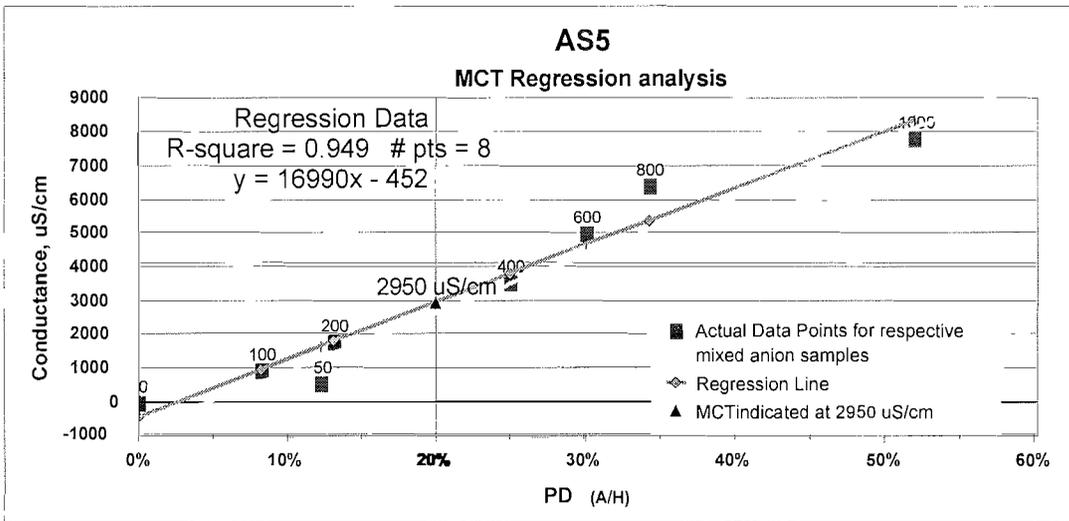
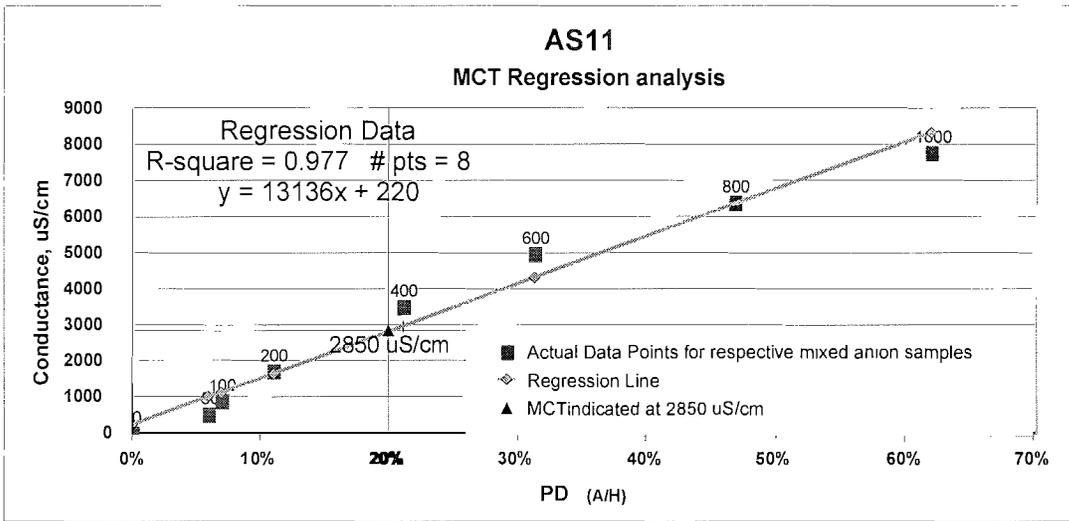
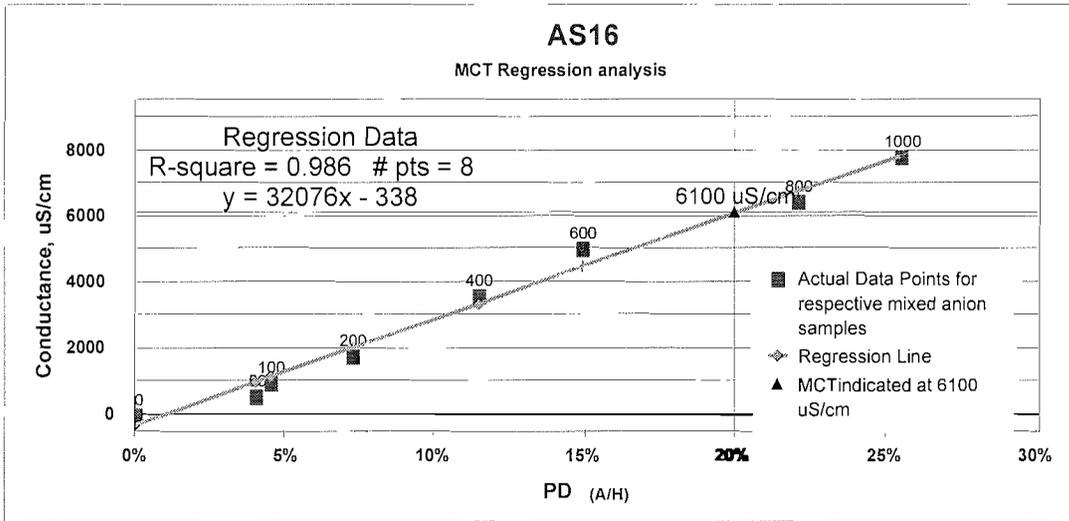


**FIGURE 4. STACKED CHROMATOGRAMS INDICATING INFLUENCE OF HIGH CONCENTRATIONS OF COMMON ANIONS ON PERCHLORATE AT 25 ug/L DURING THE MCT DETERMINATION (Conditions as indicated in Table 1)**



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JUL 2004

FIGURE 5. REGRESSION ANALYSIS OF THE MCT DETERMINATION DATA



4 DEC 2011

## Determination of trace-level perchlorate according to U.S. EPA Method 314.0 using a polyvinyl alcohol gel resin

Brian M. De Borja and Derrick W. Rowe

In the environment, perchlorate may exist as the salt of ammonium, potassium, or sodium. It is known to be highly mobile in aqueous systems and may persist for several decades under typical groundwater and surface water conditions. Ammonium perchlorate is commonly manufactured for use in solid propellant for rockets, missiles, and fireworks.<sup>1</sup> As a result of its limited shelf life, large amounts of the chemical have been disposed of in California and possibly other areas since the 1950s.<sup>2</sup> Another possible source of perchlorate contamination has been linked to chemical fertilizers.<sup>3</sup>

In the last three years, perchlorate has been found in the water supplies of over 15 million people in California, Nevada, and Arizona and in surface or groundwater in other parts of the country (Utah, Texas, West Virginia, Arkansas).<sup>3</sup> However, the extent of the problem is still unknown and other states may likely be affected. In California, the contamination of perchlorate has become a serious problem. To date, nearly 2200 drinking water sources and 382 public water systems have been tested for the presence of perchlorate. The results from this study indicate the detection of the chemical in 185 drinking water sources and 55 public water systems.<sup>4</sup>

The presence of perchlorate in the environment is a serious health concern due to its ability to affect the normal uptake of iodide by the thyroid gland.<sup>1</sup> Perchlorate is also considered a possible carcinogen.<sup>5</sup> Currently, there is no National Primary Drinking Water Regulation (NPDWR) for perchlorate. In 1996, perchlorate was placed on the Contaminant Candidate List, which is not currently subject to the NPDWR.<sup>1</sup> Current data from the U.S. EPA suggests an action level from 4 to 18 µg/L in order to provide adequate human health protection.<sup>3</sup> Levels exceeding this range will require removal and proper treatment of the contaminated water source. In 1997, the California Department of Health Services (CDHS)<sup>6</sup> and the Nevada Division of Environmental Protection (NDEP)<sup>4</sup> established an action level of 18 µg/L. In 1999, Arizona and Texas set provisional action levels of 31 and 22 µg/L, respectively.<sup>3</sup>

Ion chromatography (IC) is now a well-accepted technique for the routine monitoring of inorganic anions<sup>6</sup> and more recently for perchlorate<sup>7</sup> in drinking water. The determination of perchlorate by most conventional anion exchange columns is a difficult task due to its polarizability. This results in long retention times, poor peak shapes, and reduced sensitivity. Therefore, a column should be characterized as hydrophilic for this type of analysis.<sup>7</sup> Prior to 1997, perchlorate could not be detected below 100 µg/L.<sup>3</sup> In April 1997, the CDHS developed a method using a hydroxide eluent modified with *p*-cyanophenol for the determination of perchlorate down to 4 µg/L.<sup>3,8</sup>

This article discusses an improved method for the determination of trace levels of perchlorate. The method discussed required a large sample loop with a Metrosep A Supp 5 column, a hydroxide eluent modified with *p*-cyanophenol, and suppressed conductivity to quantitate down to the 2 µg/L level. Other parameters, such as calibration linearity, method detection limit, matrix conductivity threshold, and recovery of perchlorate in various matrices will be discussed. In addition, the performance of a dedicated IC system (Metrohm 761 Compact IC, Metrohm-Peak, Inc., Houston, TX) will be discussed briefly.

### Experimental

#### Instrumentation

A Metrohm Modular IC system was equipped with a 709 pump, 732 conductivity detector, 762

software interface, 753 suppressor, 766 autosampler, and 733 separation center. The separation center included a six-port injection valve fitted with a 1000-µL sample loop and an analytical column. A 761 Compact IC was equipped with an internal pump, injection valve, column, suppressor, conductivity detector, and software interface. The results presented are from the Modular IC, unless otherwise stated. The column in this study was a Metrosep A Supp 5 (4 × 100 mm) packed with a polyvinyl alcohol gel resin with an average particle size of 5 µm. The eluent was 20 mM NaOH/4 mM *p*-cyanophenol with a flow rate of 0.7 mL/min. A conductivity meter (Model 130, Analytical Technology Inc., Orion, Boston, MA) capable of measuring conductivity levels up to 10,000 µS/cm was used to measure the conductance of all samples.

#### Reagents and standards

All solutions were prepared with house-distilled water deionized through a Milli-Q water purification system (Millipore, Bedford, MA) with a specific resistivity of 18.2 MΩ·cm. Sodium hydroxide (JT Baker, Phillipsburg, NJ), 50% wt/wt aqueous solution, and *p*-cyanophenol (95% purity, Aldrich, Milwaukee, WI) were used to prepare the eluent. Approximately 1.05 mL of 50% NaOH was combined with 0.476 g of *p*-cyanophenol in a polypropylene bottle and diluted to 1 L with deionized water to make a final concentration of 20 mM NaOH/4 mM *p*-cyanophenol. This solution was vacuum degassed to remove CO<sub>2</sub> and a drying tube containing Ascarite II<sup>®</sup> (EM Science, Gibbstown, NJ) was used to minimize CO<sub>2</sub> contamination. A 1000-mg/L stock standard of sodium perchlorate (99% purity, Sigma, St. Louis, MO) was prepared by combining 1.23 g of sodium perchlorate and diluting to 1 L with deionized water. This concentrate solution was used to prepare all working standards throughout these experiments. Sodium salts of chloride and carbonate were obtained from Aldrich and sulfate from Sigma. These salts were used to prepare high-concentration standards to study the effects of potential interferences.

#### Results and discussion

In order to reliably determine trace-level perchlorate, certain chromatographic conditions should be optimized (eluent, column, flow rate, etc.). An analytical column is acceptable as long as it is characterized as hydrophilic and other requirements are met according to U.S. EPA Method 314.0. The purpose of using a hydrophilic IC column is to allow the efficient, reproducible, and symmetrical elution of polarizable anions, such as perchlorate. This analytical column must produce symmetrical peaks with a peak gaussian factor (PGF) between 0.80 and 1.15.<sup>7</sup>

A Metrosep A Supp 5, packed with a hydrophilic polyvinyl alcohol gel resin, was used to demonstrate these requirements. The use of this high-efficiency column with 20 mM NaOH and 4 mM *p*-cyanophenol at 0.7 mL/min permitted the elution of perchlorate within 14 min. The addition of the organic modifier allowed a significant decrease in retention time (nearly 50%), resulting in an improved separation for perchlorate. The modifier resulted in only minor effects to the background conductance, after suppression, increasing the sensitivity and improving the method detection limit.

In order to accurately quantify low concentrations of perchlorate, the system was calibrated from 2 to 200 µg/L ( $r^2 = 1.0000$ ). The PGF was calculated for each calibrated standard and ranged from 0.90 to 1.00. This indicates that symmetrical peak shapes

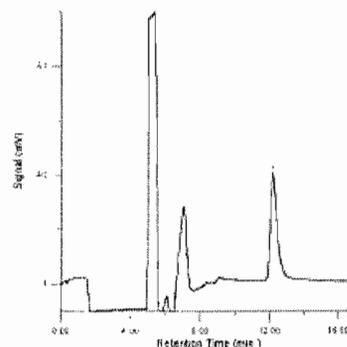


Figure 1 Chromatogram of 25 µg/L perchlorate in reagent water. Peak, 1 = perchlorate. Conditions: Metrosep A Supp 5 (4 × 100 mm), 20 mM NaOH + 4 mM *p*-cyanophenol, 0.7 mL/min, 1000 µL sample volume.

are maintained with increasing concentrations up to two orders of magnitude, permitting a reliable determination of perchlorate. Figure 1 shows a chromatogram of 25 µg/L perchlorate in reagent water using the modified conditions and column. The method detection limit (MDL) was also determined as outlined by the procedure in U.S. EPA Method 314.0. Seven replicates of a 2 µg/L perchlorate standard were analyzed over a three-day period, resulting in an MDL of 0.40 µg/L. The precision of the retention times based on the seven replicates was 0.3% RSD. The same experiment was performed on the 761 Compact IC and similar results were obtained with an MDL of 0.46 µg/L and precision of 0.7% RSD.

In some cases, sample matrices may contain high concentrations of common anions such as chloride, sulfate, and carbonate. The concentrations of these anions may be indirectly determined by monitoring the conductivity. Elevated common anion concentrations typically cause column overloading, resulting in distorted peak shapes and affecting the reliability of the results. The effect on the recovery of 25 µg/L perchlorate in a matrix containing 0–1000 mg/L of chloride, sulfate, and carbonate was examined, as shown in Table 1. Figure 2 illustrates the effect of increasing concentrations of common anions on 25 µg/L perchlorate. As demonstrated in this study, column overloading is not observed, resulting in no significant influence to the perchlorate recovery. The retention times decreased by less than 5% in the presence of 1000 mg/L of chloride, sulfate, and carbonate. However, the reduction in retention

Table 1  
The effect of high concentrations of chloride, sulfate, and carbonate on the recovery of 25 µg/L perchlorate

Common anion concentration (mg/L)*	Conductivity (µS/cm)	Perchlorate recovery (%)
0	~1	98
100	940	95
200	1800	97
400	3400	100
600	5000	89
800	6300	89
1000	7700	89

\*Common anions included chloride, sulfate, and carbonate.

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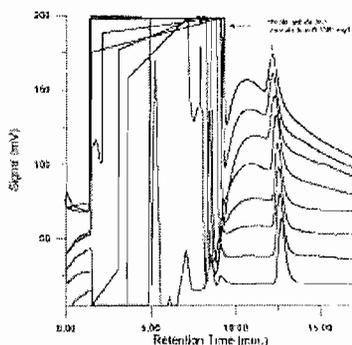


Figure 2 Stacked chromatograms of 0–1000 mg/L chloride, sulfate, and carbonate in the presence of 25 µg/L perchlorate. Peak, 1 = perchlorate. Same conditions as Figure 1.

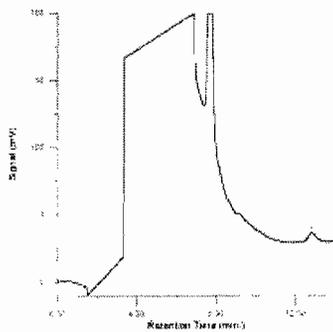


Figure 3 Drinking water from Houston, TX, spiked with 4 µg/L perchlorate. Peak, 1 = perchlorate. Same conditions as Figure 1.

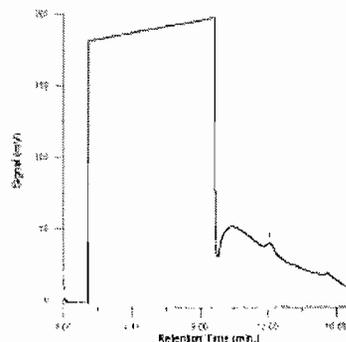


Figure 4 Chromatogram of 4 µg/L perchlorate spiked in a synthetic matrix containing 400 mg/L chloride, 500 mg/L sulfate, and 600 mg/L carbonate. Peak, 1 = perchlorate. Same conditions as Figure 1.

Table 2

Matrix	Recoveries of perchlorate at 4 and 25 µg/L spiked in various matrices			
	Matrix conductivity (µS/cm)	Spiked perchlorate concentration (µg/L)	No. replicates	Mean recovery (%)
Reagent water	~1	4	8	101
		25	8	101
Drinking water	300	4	7	89
		25	8	101
Treated wastewater	980	4	8	106
		25	8	96
Synthetic standard*	3900	4	7	103
		25	8	102

\*Synthetic standard contained 400 mg/L chloride, 500 mg/L sulfate, and 600 mg/L carbonate.

time did not affect the identification of the perchlorate peak. The highest permitted conductance (matrix conductivity threshold) using the Metrosep A Supp 5 was 7100 µS/cm, (~920 mg/L of chloride, sulfate, and carbonate). Identical results were obtained from the 761 Compact IC.

The recoveries of samples with various conductance levels spiked with 4 or 25 µg/L perchlorate were examined. The samples in this study included drinking water, treated wastewater, and a synthetic matrix containing elevated concentrations of common anions. As shown in Table 2, quantitative recoveries (89–106%) for perchlorate were obtained

for all sample matrices. Figure 3 shows a chromatogram of drinking water from Houston, TX, spiked with 4 µg/L perchlorate. In addition, a synthetic standard was used to simulate a high ionic strength field sample. The sample was prepared by combining 400 mg/L chloride, 500 mg/L sulfate, and 600 mg/L carbonate to a matrix spiked with perchlorate. Figure 4 shows a chromatogram of 4 µg/L perchlorate in the presence of the synthetic matrix. The results demonstrated that the various matrices examined do not significantly influence the recovery of perchlorate. The column capacity provides more economical determination of trace-level perchlorate by reducing the need for sample preparation cartridges.

#### Conclusion

The use of a polyvinyl alcohol gel resin such as the Metrosep A Supp 5 with modification of the eluent provides efficient and reliable determination of trace-level perchlorate. The column capacity allowed quantitative recoveries for low µg/L perchlorate in highly conductive matrices. The high matrix conductivity threshold of 7100 µS/cm reduces the need for off-line sample preparation cartridges. The method detection limits of 0.40 and 0.46 µg/L for the modular and compact IC system, respectively, allow quantitation significantly below the set action level by the U.S. EPA. Experiments are currently being performed to further evaluate polyvinyl alcohol gel resins for determining polarizable anions, such as perchlorate.

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PERCHLORATE in WATER by ION CHROMATOGRAPHY  
Modified <sup>a</sup> EPA Method 300.0 (Revision 2.1, August 1993)

**Table 1. Summary of Contract Required Detection Limits, Holding Times, and Preservation for Perchlorate**

Analytical Parameter	Contract Required Detection Limit (CRDL)	Technical and Contract Holding Times	Preservation
Perchlorate	5.0 µg/L	Technical: 28 days from collection; Contract: 21 days from receipt at laboratory	Cool to 4°C ±2°C

<sup>a</sup> EPA Method 300.0 modified for the analysis of perchlorate in water as described in the California Department of Health Services (DHS) method (Sanitation & Radiation Laboratories Branch; Determination of Perchlorate by Ion Chromatography, Rev. No. 0, June 3, 1997).

**Data Calculations and Reporting Units:**

Calculate the sample results according to Section 12 of EPA Method 300.0 (Revision 2.1, August 1993) or Section 12 of the California DHS method. Report sample results in the concentration unit of micrograms per liter (µg/L). Report perchlorate concentrations which are ≥10 µg/L to three significant figures and perchlorate concentrations which are <10 µg/L to two significant figures.

For rounding results, adhere to the following rules:

- a) If the number following those to be retained is less than 5, round down;
- b) If the number following those to be retained is greater than 5, round up; or
- c) If the number following the last digit to be retained is equal to 5, round down if the digit is even, or round up if the digit is odd.

All records of analysis and calculations must be legible and sufficient to recalculate all sample concentrations and QC results. Include an example calculations in the data package.



Table 2. Summary of Calibration Procedures for Perchlorate by Modified EPA Method 300.0

Calibration Element	Frequency	Acceptance Criteria	Corrective Action
Initial Calibration (minimum blank + 5 points for perchlorate) (ICAL) <sup>a, b</sup>	Initially; monthly; or whenever required due to failure of IPC	$r \geq 0.995$	1. Terminate anal 2. Recalibrate an sample analysis
Instrument Performance Check (IPC) <sup>c</sup> (Separate source from ICAL standards)	Following the calibration and prior to sample analysis; after every 10 samples; and end of run	$\pm 10\%$ from expected concentration	1. Recalibrate an 2. Reanalyze samp good IPC
Retention time evaluation for IPC standard	Each analysis of IPC standard	$\pm 10\%$ from expected retention time	1. Recalibrate an 2. Reanalyze samp good IPC
Calibration Blank Verification (ICB, CCB)	After ICAL; every IPC; and end of the analytical sequence	$< \text{CRDL}$	1. Terminate anal 2. Identify and d 3. Recalibrate, v all associated sa
CRDL Verification Standard	After initial IPC/CCB	$\pm 20\%$ from expected concentration	1. Reprep and rea 2. Recalibrate an

<sup>a</sup> The low level standard should be at a concentration equal to the contract required detection limit (CRDL).

<sup>b</sup> Report the retention time window for each analyte. Determine retention time windows as  $\pm 10\%$  of the mean retention time for each analyte in the calibration standards.

<sup>c</sup> The IPC standard solution should contain perchlorate at a concentration different from the concentration of perchlorate in the calibration standards.

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Table 3. Summary of Internal Quality Control Procedures for Perchlorate by Modified EPA Method 300.0

QC Element	Frequency	Acceptance Criteria	Corrective Action
Laboratory Reagent Blank (LRB)	One per Batch or SDG <sup>a</sup> (1 per 20 samples minimum)	< CRDL	1. If lowest sample c than 10X the blank co 2. If samples are non 3. If detected sample less than 10X blank c samples must be prepa another method blank
Duplicate Sample (DUP)	One per batch or SDG (1 per 20 samples minimum)	RPD <20% for samples >5X CRDL; $\pm$ CRDL for samples <5X CRDL	1. Flag associated da
Laboratory Fortified Matrix (LFM) <sup>b</sup>	One per batch or SDG (1 per 20 samples minimum)	$\pm$ 25% from expected value	1. Flag associated da
Laboratory Fortified Blank (LFB)	One per batch or SDG (1 per 20 samples minimum)	$\pm$ 10% from expected concentration	1. Terminate analysis 2. Identify and docum 3. Reanalyze all asso

<sup>a</sup> SDG - Sample Delivery Group - each case of field samples received; or each 20 field samples within a case; or each 14 calendar day period during which field samples in a case are received.

<sup>b</sup> If the LFM sample exceeds the calibration range, the sample must be diluted appropriately, re-spiked, and reanalyzed.

Dilute and reanalyze samples with concentrations exceeding the range of the calibration curve. Results for such reanalyses should fall within the mid-range of the calibration curve. Report results and submit documentation for both analyses.

Perform confirmatory techniques, such as sample dilution and spiking, when the identification of a peak in the chromatogram is questionable. Spike the sample with an appropriate amount of the relevant standard and reanalyze.

Analyze a laboratory blank after the analysis of an unusually concentrated sample to check for contamination by carry-over. Any sample with perchlorate present at a concentration 2x the calibration range is considered an unusually concentrated sample.


  
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