6161 Vol 1 of 2

Final Quality Assurance Project Plan

Fort Devens, Massachusetts

Volume I

Submitted to

U.S. Army Environmental Center (USAEC)
Formerly USATHAMA
Aberdeen Proving Ground, Maryland

Revision 1
June 16, 1993

Arthur D. Little, Inc.
Acorn Park
Cambridge, Massachusetts
02140-2390

ADL Reference 67064(5)

DAAA15-91-D-0016

Note: Title pages for specific Delivery Orders are provided as supplemental supplements to this Quality Assurance Project Plan.

AEC Form 45, 1 Feb 93 replaces THAMA Form 45 which is obsolete.

Final Quality Assurance Project Plan

Arthur D Little

Fort Devens, Massachusetts

Program Manager, Robert Lambe — 16 JUN 93 Date

Program Quality Assurance Officer, Stuart Canton — 6/17/93 Date

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ABERDEEN PROVING GROUND, MD.

Forward

This Quality Assurance Project Plan (QAPjP) is designed to provide general coverage of a broad range of quality assurance issues in support of activities associated with site investigations, evaluations, and studies at Fort Devens, Massachusetts. These activities are carried out as required in Delivery Orders awarded under the Arthur D. Little TEPS Contract DAAA15-91-D-0016 with the U.S. Army Environmental Center (USAEC). This QAPjP documents items that are general to work being undertaken at Fort Devens. Delivery Order specific information is provided in supplements to this QAPjP. These supplements incorporate the more general information by reference.

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List of Acronyms and Abbreviations

AAS	Atomic Absorption Spectroscopy
ADL	Arthur D. Little, Inc.
AR	Analytical Reagent
ASL	Active Sanitary Landfill
ASTM	American Society for Testing and Materials
BCRA	Base Closure and Realignment Act
BFB	Bromofluorobenzene
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFD	Clean Fill Dump
CFR	Code of Federal Regulations
CLP	Contract Laboratory Program
CNCL	Cyanogen Chloride
COC	Chain-of-Custody
COR	Contracting Officer's Representative
CRL	Certified Reporting Limit
CV	Cold Vapor
DFTPP	Decafluorotriphenylphosphine
DL	Detection Limit
DPDO	Defense Property Disposal Office
DSY	DPDO Salvage Yard
ECD	Electron Capture Detector
EOD	Explosive Ordnance
EPA	United States Environmental Protection Agency
FID	Flame Ionization Detector
FS	Feasibility Study
FSP	Field Sampling Plan
FTA	Fire Training Area
GC/FID	Gas Chromatography/Flame Ionization Detector
GC/MS	Gas Chromatography/Mass Spectometry
GC	Gas Chromatography
GC/ECD	Gas Chromatography/Electron Capture Detector
GFAA	Graphite Furnace Atomic Absorption Spectrophotometer
HCL	Hydrochloric Acid
HCN	Hydrocyanic Acid
HHA	Helicopter Hangar Area
HNU	HNU Inc., Manufacturer of Photoionization Detector
HPLC	High Performance Liquid Chromatograph(y)
IAG	Interagency Agreement
IC	Ion Chromatograph(y)

ICAP	Inductively Coupled Plasma-Emission Spectroscopy
IL	Inactive Landfill
IR	Installation Restoration
IRDMIS	Installation Restoration Data Management Information System
IRP	Installation Restoration Program
LCL	Lower Control Limit
LEL	Lower Explosivity Limit
LOF	Lack of Fit
LWL	Lower Warning Limit
MEP	Master Environmental Plan
MRD	Missouri River Division (U.S. Army Corps of Engineers)
MS	Mass Spectrometry
MS/MSD	Matrix Spike/Matrix Spike Duplicate
MTR	Minimum Testing Range
NA	Not Analyzed
NCP	National Contingency Plan
NCR	Non Conformance Record
ND	Not Detected
NIST	National Institute of Standards and Technology
No.	Number
ODA	Ordnance Demolition Area
OSHA	Occupational Safety and Health Administration
OVA	Organic Vapor Detector
PA	Preliminary Assessment
PCB	Polychlorinated Biphenyls
PID	Photoionization Detector
PRI	Potomac Research, Inc.
PWRC	Patuxent Wildlife Research Center
QA/QC	Quality Assurance/Quality Control
QAPjP	Quality Assurance Project Plan
RCRA	Resource Conservation and Recovery Act
RI	Remedial Investigation
RI/FS	Remedial Investigation/Feasibility Study
RIA	Remedial Investigation Addendum
ROD	Record of Decision
RPD	Relative Percent Difference
SA	Study Area
SARM	Standard Analytical Reference Material
SI	Site Investigation
SIA	Site Investigation Addendum
SLI	Site Location Identity
SOP	Standard Operating Procedure
SOW	Statement of Work

SRM	Standard Reference Materials
SW	Solid Waste
TAL	Target Analyte List
TCL	Target Compound List
TCLP	Toxicity Characteristic Leaching Procedure
TDS	Total Dissolved Solids
TEPS	Total Environmental Program Support
TIC	Tentatively Identified Compounds
TOC	Total Organic Compounds
TPHC	Total Petroleum Hydrocarbons
TSS	Total Suspended Solids
UCL	Upper Control Limit
USACE	U.S. Army Corp of Engineers
USAEC	United States Army Environmental Center
USATHAMA	U.S. Army Toxic and Hazardous Materials Agency
USC	Unique Sample Code
UV	Ultraviolet
UWL	Upper Warning Limit
UXO	Unexploded Ordnance
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound
WQP	Water Quality Parameters
ZI	Zero Intercept

1.0 Project Description

1.1 Introduction

This Quality Assurance Project Plan (QAPjP) has been prepared to address activities associated with investigations, evaluations, and studies at Fort Devens, Massachusetts. It has been prepared for the U.S. Army Environmental Center (USAEC) to fulfill the requirement of deliverable ELIN A004 under specific Delivery Orders under the TEPS contract DAAA15-91-D-0016. This QAPjP has been developed in accordance with *USATHAMA Quality Assurance Program*, USATHAMA *Geotechnical Requirements*, and *Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA*.

Arthur D. Little's Corporate Policy includes a commitment to a high standard of quality in the work it performs for and delivers to its clients. Our commitment to quality is reflected in our general policies and procedures (hiring practices, performance evaluations, project management and control tools, and technical review procedures) and also in specific, written Quality Assurance Program and Project Plans that we develop and implement for major new assignments that we undertake. We expect similar commitment to quality from our subcontractors.

The objective of the *USATHAMA Quality Assurance Program* is to establish a Quality Assurance (QA) system and proper Quality Control (QC) procedures. The *USATHAMA Quality Assurance Program* defines QA as "the system whereby an organization provides assurance that monitoring of quality related activities has occurred" and QC as "specific actions taken to ensure that system performance is consistent with established limits. It is these actions which ensure accuracy, precision, and comparability of results." This QAPjP is designed to address a broad range of quality assurance issues at a specific location, Fort Devens, Massachusetts. Delivery Order specific information is provided in the supplements to this QAPjP. The QAPjP with the Delivery Order Specific supplements is developed to address QA/QC activities. These activities ensure that the results of the field investigation program are properly documented and of adequate quality to support decisions about the necessity for and nature of further investigations and remedial actions.

This QAPjP for work at Fort Devens has been developed to comply with the requirements of the *USATHAMA Quality Assurance Program*, PAM 11-41, Revision No. 0, January 1990. We will be using a subcontracted U.S. Army Corps of Engineers Missouri River Division (MRD) validated laboratory, DataChem Laboratories of Salt Lake City, Utah, for chemical analyses of samples collected during the Fort Devens Investigation. Therefore, we have attached the Quality Assurance Program Plan from DataChem to this QAPjP. The DataChem plan

describes specific laboratory QA/QC activities, while our plan describes Arthur D. Little QA/QC activities, including sufficient details to assure, through reviews, that laboratory results meet USAEC requirements.

This QAPjP with Delivery Order Specific supplements is one of the technical plans developed for each Delivery Order, which may include Work Plans and Health and Safety Plans that were prepared as separate documents.

1.2 Site Background

1.2.1 Site Description

Fort Devens is located in Worcester and Middlesex Counties, approximately 40 miles west of Boston, Massachusetts, in the vicinity of the town of Ayer (Figure 1-1). The study areas for specific Delivery Orders are provided in the supplements. Figure 1-2 shows the regional setting of Fort Devens. The installation includes portions of the towns of Ayer, Harvard, Lancaster, and Shirley. In 1917, approximately 11,000 acres were leased to establish Camp Devens. Between 1919 and 1923, approximately 4,900 acres were purchased. In June 1940, Fort Devens received permission to acquire more land, and, by 1941, the total land area increased to 10,163 acres.

Since 1955, various land parcels, ranging in size from 1 to 662 acres, have been excessed by Fort Devens. The more recent transactions included the 662 acres for the Oxbow National Wildlife Refuge, excessed in 1972 to the Department of the Interior; 76.5 acres deeded to the Town of Ayer in 1978; and an additional 57.26 acres, excessed in 1988. Fort Devens currently covers approximately 9,280 acres, consisting of the Main, North, and South Post areas. Massachusetts Highway 2 crosses Fort Devens and separates the Main Post from the South Post.

The majority of the facilities at Fort Devens lie within the Main Post, located north of Massachusetts Highway 2. The Main Post provides all of the on-post housing, including over 1,700 family units and 9,800 bachelor units (barracks and unaccompanied officers' quarters). Other facilities on the Main Post include community services (e.g. the shoppette, cafeteria, post exchange, bowling alley, golf course, and hospital), administrative buildings, classroom and training facilities, maintenance facilities, and ammunition storage.

The terrain surrounding Fort Devens includes rolling areas and wooded hills. Fort Devens is located in the Nashua River Basin, and approximately 8 miles of the river, running from south to north, lie within the reservation boundaries (Figure 1-2). One lake and several ponds are located within Fort Devens. Land surface elevations

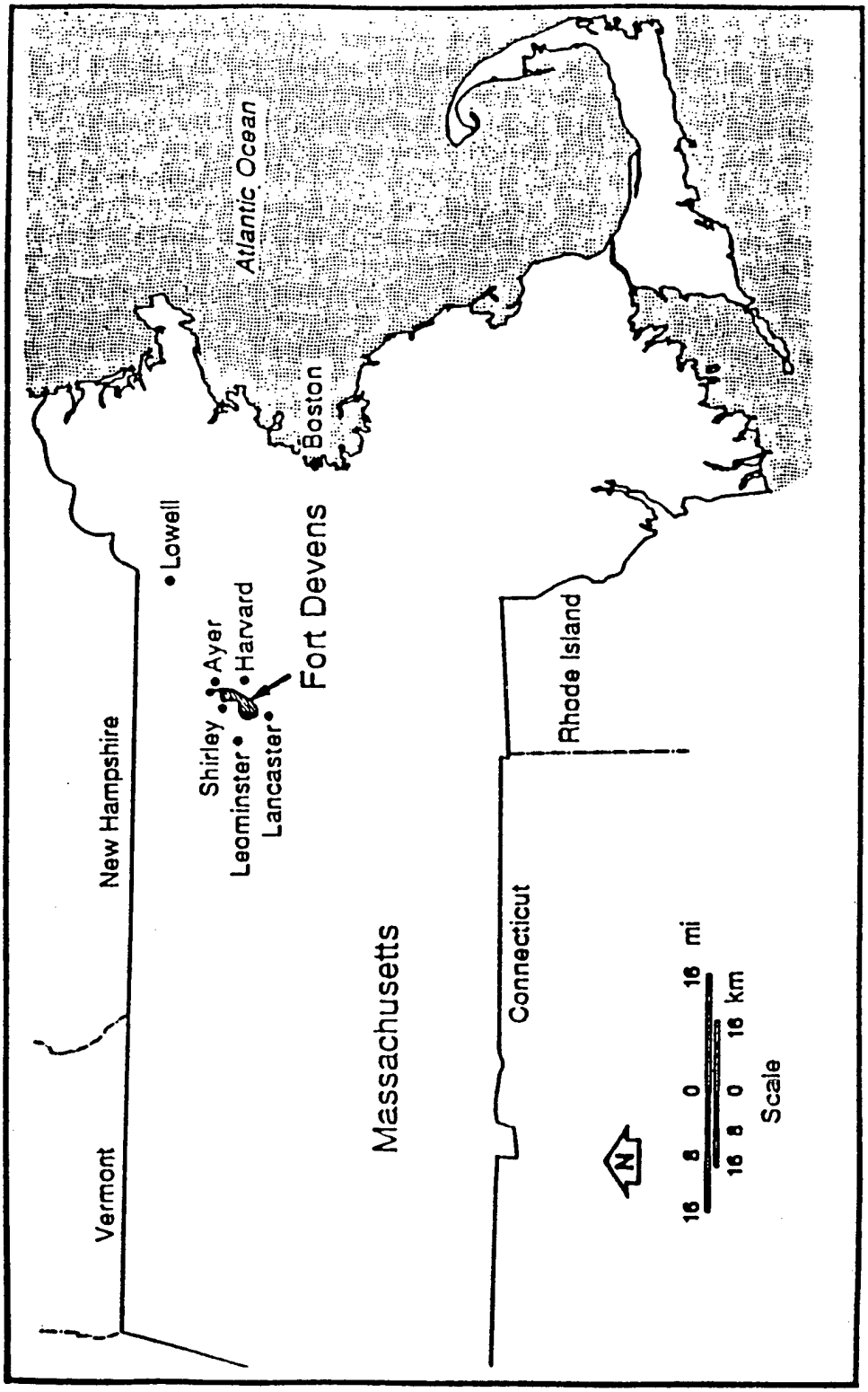
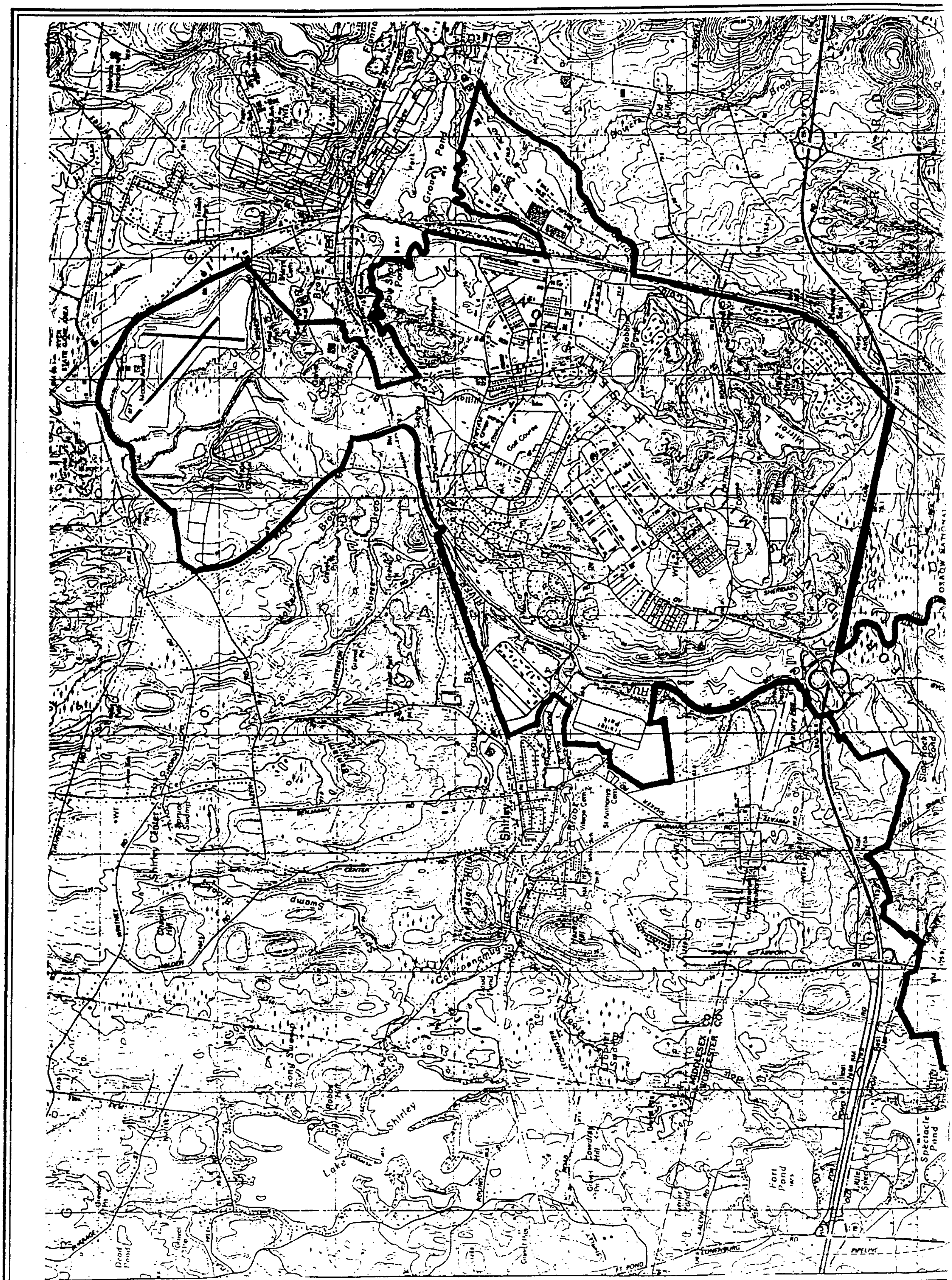
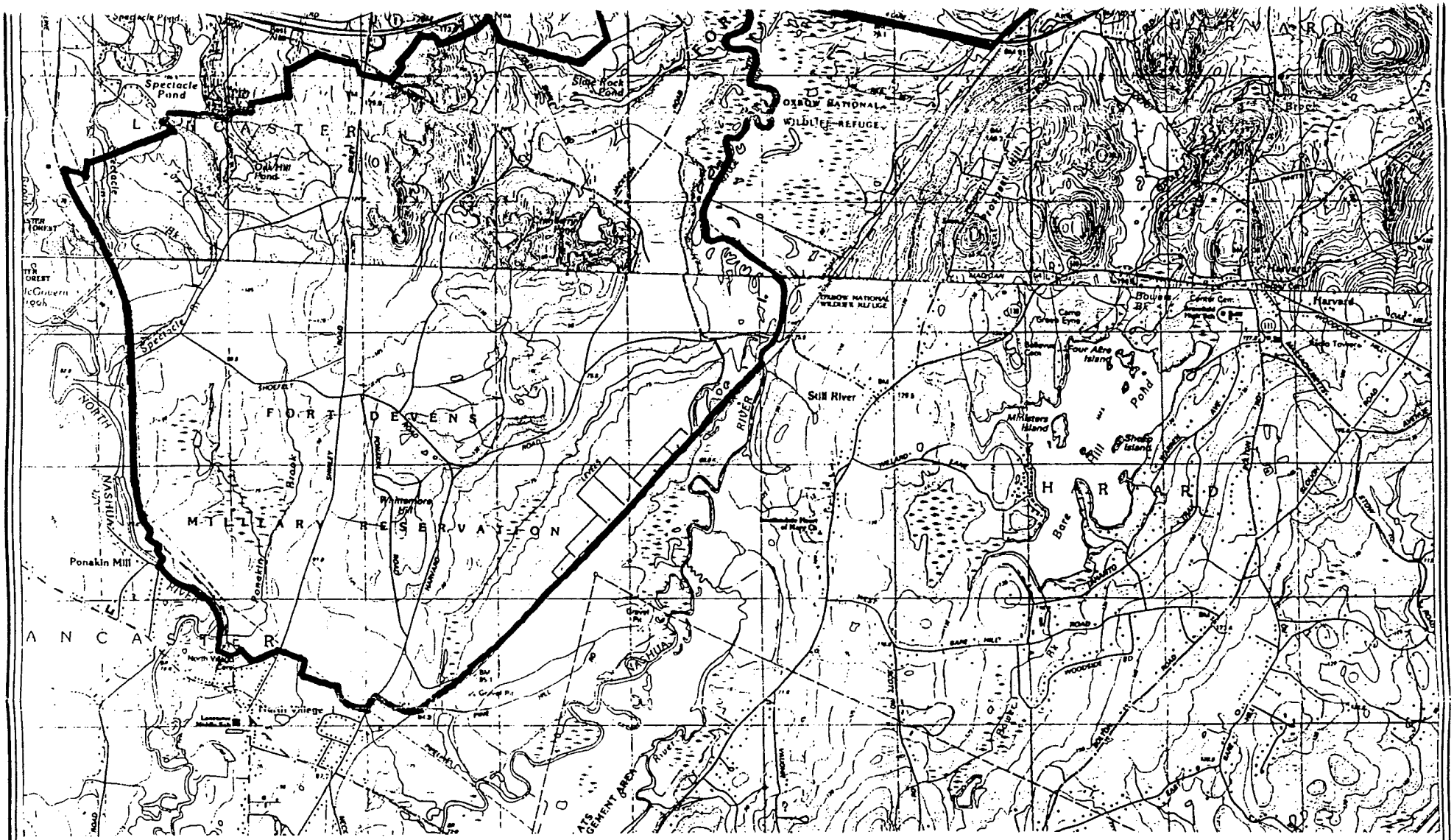


Figure 1-1: Location of Fort Devens in Massachusetts (Source: Adapted from McMaster et al. 1982)


Golf Course
Shirley
Lake
Shirley
Swamp
Fort Pond
MIDDLESEX CO
WORCESTER CO



PREPARED FOR: USAEC			SOURCE: USGS TOPOGRAPHIC 7.5–MINUTE SERIES; AYER, MASSACHUSETTS, 1988, AND HUDSON, MASSACHUSETTS, 1988	TITLE: **Figure 1-2** REGIONAL SETTING OF FORT DEVENS
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within Fort Devens range from about 200 feet above mean sea level (MSL) along the Nashua River on the northern boundary to 450 feet above MSL in the southern portion of the installation.

1.2.2 Site History

Camp Devens was established in 1917 as a temporary training camp for soldiers from the New England area. Peak military strength during the World War I era was 38,000. Since that time, it has been an installation of the U.S. Army Forces Command (FORSCOM). In 1929, Camp Devens was designated a summer training camp for several military groups. By 1931, Camp Devens became a permanent post and was renamed Fort Devens. Between 1929 and 1930, it served as the location for test firing of rockets. Between 1931 and 1940, Fort Devens functioned as a training installation.

From November 1940 until May 1946, Fort Devens provided an induction center for an estimated 650,000 people in response to World War II. At the close of World War II, Fort Devens served as a demobilization center and was subsequently placed on caretaker status. It was again used as an induction and training center during the Korean and Vietnam conflicts.

Currently, the mission of Fort Devens is to command and train its assigned duty units and to support the U.S. Army Security Agency Training Center and School, U.S. Army Reserves, Massachusetts National Guard, Reserve Officer Training Programs, and Air Defense sites in New England. No major industrial operations occur at Fort Devens, although several small-scale industrial operations are performed under 1) the Directorate of Plans, Training, and Security; 2) the Directorate of Industrial Operations (DIO); and 3) the Directorate of Engineering and Housing (DEH). The major waste-producing operations performed by these groups are photographic processing and maintenance of vehicles, aircraft, and small engines.

As a result of the Base Realignment and Closure (BRAC) Act of 1991, Fort Devens has been designated as a BRAC 91 installation. The on-going Installation Restoration Program will be supplemented by environmental restoration activities in preparation for base closure; these activities are required to meet the requirements of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980 and Superfund Amendments and Reauthorization Act (SARA) of 1986.

1.2.3 Previous Investigations

In August 1982, an installation assessment (preliminary assessment) of Fort Devens was conducted. No additional CERCLA related studies were recommended. In 1985, a Solid Waste Management Unit Report was prepared for Fort Devens to identify possible solid waste management units (SWMUs) as part of the Resource

Conservation and Recovery Act (RCRA) Part B permit for the Fort Devens hazardous waste storage facility. Forty SWMUs were identified. Action was recommended at 10 of the SWMUs, which included the Shepley's Hill Landfill (No. 1) and Cold Spring Brook Landfill.

In order to define areas requiring investigation, to outline types of studies required, and to assist the Army with continuity in the Fort Devens project, a Master Environmental Plan (MEP) was initiated in 1988. Fort Devens was subsequently placed on the National Priorities List (NPL) on December 21, 1989. The listing of Fort Devens as an NPL site was a result of volatile organic contamination in the ground water at the Shepley's Hill Landfill (No. 1), metal contamination in the ground water at the Cold Spring Brook Landfill, and the close proximity of both locations to public water supplies. After listing of the site, work on the MEP was halted until the Federal Facilities Interagency Agreement (IAG) could be developed. A two-party IAG was signed by the Army and the U.S. Environmental Protection Agency (EPA), Region I, on May 13, 1991 and finalized on November 15, 1991. The IAG is the framework for the implementation of the CERCLA/SARA process at Fort Devens. Work on the MEP was resumed after development of the IAG, and the regulatory draft final was submitted for review on November 29, 1991. The interrelationship between the Army's IRP and the CERCLA/SARA process is delineated in the MEP.

With the inclusion of Fort Devens on the Defense Secretary's BRAC 91 list, an Enhanced Preliminary Assessment (PA) was required to address areas not normally included in the CERCLA process, but that required review prior to closure. While the Enhanced PA addresses MEP activities, its focus was to determine whether or not additional areas require detailed records review and site investigation and to provide information and procedures for the investigation of installation wide areas requiring environmental evaluation. The enhanced PA also addressed closure of RCRA regulated units and RCRA corrective actions.

1.3 Task Objectives and Scope of Work

The objectives and scope of work for each Delivery Order are provided in the supplements.

1.4 Applicability

This Quality Assurance Project Plan (QAPjP) with Delivery Order Specific supplements is applicable to both the analytical and the field investigation component of the task order.

QA refers to the system whereby an organization provides assurance that monitoring of quality-related activities has occurred; QA is generally interpreted as a recordkeeping system for documentation of activities including traceability, completeness, and security of documents. Through implementation of this QA program in the field, in the office, and at the laboratory, the validity and reliability of site data and other documents will be monitored such that the adequacy of the data or documents can be substantiated. QC refers to specific actions taken to verify that activities performed are consistent with established limits of acceptable quality. It is through these actions that accuracy, precision, and comparability of results are verified. QC activities must be conducted within a QA program to document that QC exists.

This QAPjP establishes a QA system and appropriate QC procedures for use by Arthur D. Little and its subcontractors. The emphasis of this plan is on activities that generate field and analytical data; the plan also addresses field activities that may affect that integrity of these data. This plan documents specific instructions for environmental sampling and chemical analyses; requirements for all chain-of-custody procedures, and field activities; QC of computer and document-related activities; and QC of final calculations. Arthur D. Little and its subcontractors will adhere to the procedures stated in this QAPjP.

1.5 Organization of Document

This QAPjP has been prepared using the guidance provided in the *USATHAMA Quality Assurance Program Manual* (January 1990); the Plan has been organized into the sections indicated in the guidance document. The Delivery Order Specific supplements are organized into the same sections as the QAPjP. References are made to each, as appropriate. Sections 1.0 through 3.0 of this plan provide an overview of the project scope, organization and objectives. Section 1.0 provides a description of the project, project objectives, and scope of the current investigation. Section 2.0 presents the organization of the project team and identification of specific QA responsibilities. The QA objectives for the data collected during this investigation are provided in Section 3.0.

Sections 4.0 through 9.0 provide details of the procedures for sample collection and analysis and data reporting. The specific sampling procedures to be used in the collection of field samples for Fort Devens Delivery Orders are provided in Section 4.0. The sample custody procedures, for both field and laboratory activities, are summarized in Section 5.0. Section 6.0 provides the required calibration procedures for the field and laboratory instruments to be used. Section 7.0 specifies the procedures for field and laboratory data collection; most of the analytical procedures to be used for the Fort Devens project are USAEC-approved methods.

The procedures to be followed for data reduction, validation, and reporting are provided in Section 8.0; these procedures conform with the USAEC IRDMIS requirements. Section 9.0 identifies the QA procedures internal to the sample collection and analysis activities and specifies the frequency for each of these checks.

Section 10.0 summarizes the performance and system audits to be conducted within this investigation. Section 11.0 addresses the procedures and schedule for preventive maintenance of field and laboratory instrumentation. The specific procedures routinely used to assess data quality (precision, accuracy and completeness) are provided in Section 12.0; for the USAEC-approved methods, these procedures are specified within the method and the calculations are performed using the USAEC software. Recommended corrective actions and QA reports to management are addressed in Sections 13.0 and 14.0, respectively.

A Glossary of Terms and List of Acronyms is provided at the beginning of the plan immediately following the Table of Contents. In addition, three Appendices have also been included. Appendix A provides QA Program Plan for USAEC, prepared by DataChem Laboratories, Inc.; Appendix B provides a checklist to be used during field and laboratory activities to assure compliance with this QA Plan; and Appendix C includes copies of the non-USAEC methods.

Delivery Order Specific supplements are provided at the end of this document.

2.0 Project and QA/QC Organization and Responsibilities

This section describes the general organizational structure for the Fort Devens investigations being conducted by Arthur D. Little. This structure indicates the overall assignment of responsibility for all aspects of the project and the functional and communication relationships among the organizational elements participating in this project. The general organizational structure for Fort Devens investigations is presented in Figure 2-1. Delivery Order Specific assignments, roles, and responsibilities are provided in the supplements. The roles and responsibilities of key project team personnel are as follows.

2.1 Project Organization

2.1.1 Program Manager

Dr. Robert N. Lambe is the Arthur D. Little Program Manager for the USAEC Total Environmental Program Support (TEPS) contract and will be responsible for: monitoring technical progress; reviewing and approving all work products; reviewing and approving all deliverables before submission to USAEC; monitoring financial and schedule control; and instituting corrective action, if necessary.

2.1.2 Task Manager

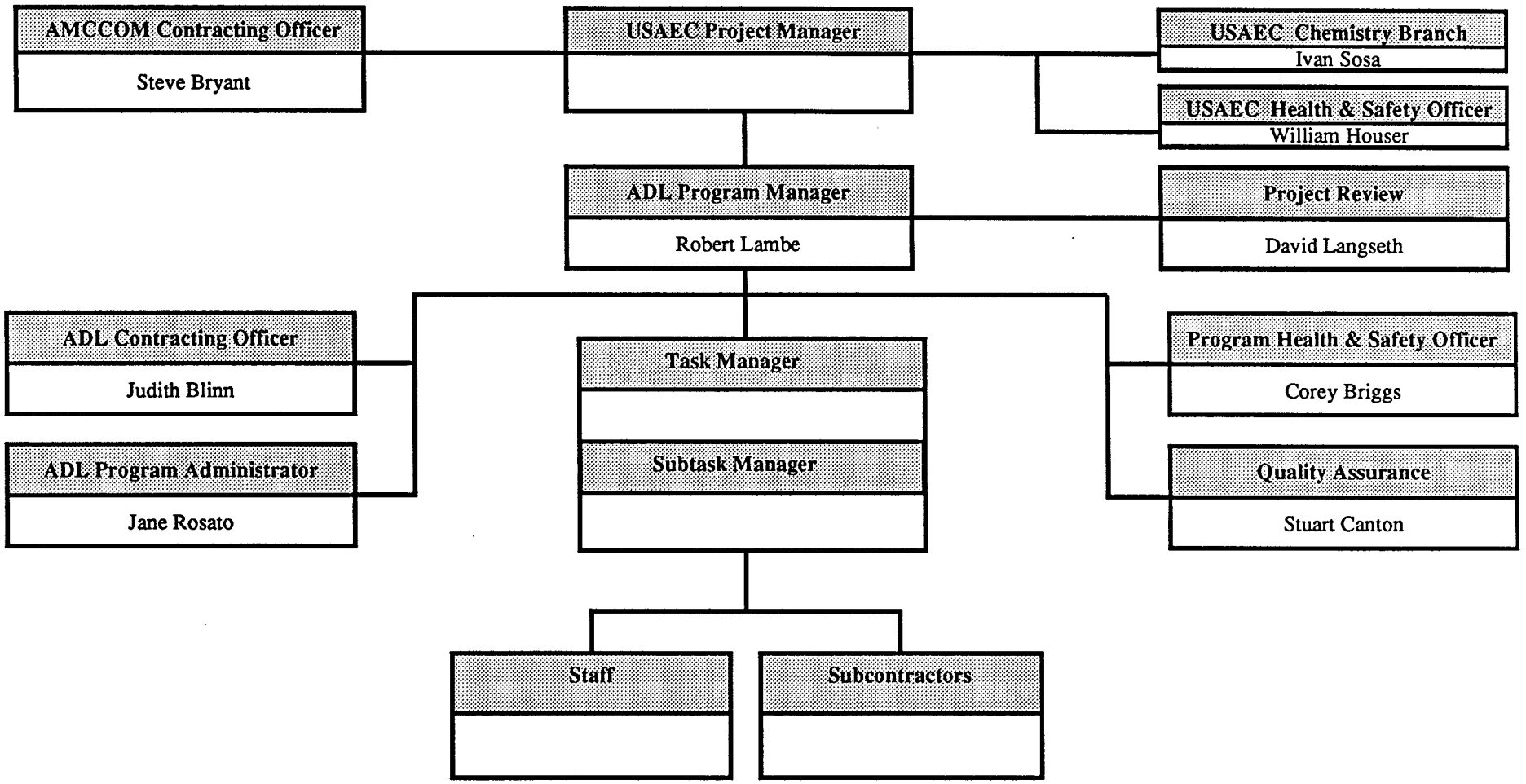
The Arthur D. Little Task Manager for specific Delivery Orders will work directly with Dr. Lambe. As Task Manager, his/her responsibilities include: project staffing and direct management of all staff assigned to the Delivery Order; direct financial and schedule control; review and approval of all deliverables; recommending corrective actions, if necessary, to the Program Manager; and maintaining a liaison with the USAEC Contracting Officer Representative and Fort Devens Environmental Office Manager. In this role, the Task Manager will be responsible for ensuring that the USAEC Project Officer and Fort Devens Environmental Office Manager are kept informed of all technical progress as necessary.

2.1.3 Task Staff

Subtask Managers are assigned to specific Delivery Orders as required by the scope of work.

The Subtask Managers are responsible for coordinating all phases of activities required to complete the stated goals of their Subtask assignment, including tracking and reporting on technical quality, schedule, budget, deliverables, problems, and corrective actions. Subtask Managers are responsible for ensuring that the Task Manager is kept informed of all technical progress and potential problem areas.

Figure 2-1
Fort Devens Organizational Chart



Consistency in approach for each Subtask will be assured through management by the Task and Subtask Managers, brief weekly meetings, and use of a common resource base to perform the specific work assignments. Technical staff members will take direction from the Subtask Managers.

Field activities will be managed by a Subtask Manager. During on-site field investigations at Fort Devens, the field team will include a site coordinator who will be the Subtask Manager or his/her designee and a designated on-site Health and Safety supervisor. In addition to field geologists and technicians, subcontractors, which could include UXO survey, drilling, and the elevation/location survey contractors, will also report to the site coordinator.

Laboratory activities will be overseen by the Lead Chemist, Ms. Mary Kozik. She or her designee will be responsible for coordinating field and laboratory activities, and reviewing our subcontracted laboratory, DataChem, operations and data files/packages.

Dr. David E. Langseth, Vice President in charge of Earth Sciences and Engineering, will serve as Technical Reviewer, serving USAEC in two ways. First, he will provide a high level of corporate attention to the task to ensure the availability of staffing to complete the Delivery Order within the proposed schedule. Secondly, because Dr. Langseth is an engineer who has spent considerable time evaluating and selecting technologies for site remediation and hazardous waste treatment, he will provide the Army with a technical review as well as a managerial review.

2.2 Arthur D. Little QA/QC Organization

The principal responsibilities for implementing the requirements of the QAPjP will be the managers and staff for the TEPS program and specific Delivery Orders. In addition, however, we have assigned QA/QC oversight, review, and reporting responsibilities to the Program QA Officer, in addition to specific responsibilities for QA in our subcontracted laboratory. These responsibilities are described below.

2.2.1 Program QA Officer

Arthur D. Little's Total Quality Management (TQM) Program is under the direction of Dr. Alfred E. Wechsler, Senior Vice President and Chief Professional Officer. Dr. Wechsler has selected Mr. Stuart Canton as the Program Quality Assurance Officer for the USAEC TEPS Contract. In his role as an independent evaluator of Arthur D. Little's performance during this Delivery Order, Mr. Canton will report directly to Dr. Wechsler. If needed, as directed by Dr. Wechsler, he also has the authority to discuss QA/QC issues with officials at USAEC and other U.S. Army officials in the chain of command. Mr. Canton's findings and recommendations will

be communicated directly to Dr. Lambe, Program Manager, the Task Manager, and Dr. Wechsler, Chief Professional Officer during the course of Fort Devens Delivery Orders.

The primary focus of the Project Quality Assurance Officer will be that systems are in place and adequate to maintain the maximum level of quality throughout all aspects of the project.

Specific functions and duties of the Program Quality Assurance Officer include:

- Reviewing and approving of QA policies and procedures;
- Reporting the adequacy, status, and effectiveness of the QA program on a regular basis to the program management;
- Maintaining responsibility for documentation of corporate QA records, documents, and communications;
- Conducting field audits;
- Coordinating with the Lead Chemist to ensure QC procedures specific to the laboratory and data management are followed and documented.

The purpose of the field audits is to ensure that sampling and related activities are conducted in a manner consistent with the QA Program and other USAEC guidelines. This responsibility includes visiting the site to inspect sampling where applicable. Coordination with the Arthur D. Little Lead Chemist prior to the inspection is acceptable. The inspections will try to review each major type of sampling (e.g., ground water, surface water, soil, sediment) at least once per installation investigation. The visit should occur as close as possible to the first sampling effort for each matrix. Additional inspections may occur at the discretion of the Program QA Officer, with approval of the USAEC Project Officer and Arthur D. Little Task Manager. The Program QA Officer will document (Appendix U of the *USATHAMA Quality Assurance Program*, January 1990) each inspection and ensure that procedures described in the Scope of Work Project Work Plan, and QAPjP are followed. The Program QA Officer has the authority to require resampling of any site whose sampling integrity was determined to have been affected by faulty sampling procedures, after obtaining approval from the USAEC Project Officer or the Contracting Officer's Representative.

2.2.2 Lead Chemist

Arthur D. Little's Lead Chemist is Ms. Mary Kozik. She will assist with oversight of the laboratory activities for this project. Specific functions and duties include:

- Maintaining copies of our subcontracted laboratory documentation, including USAEC-approved methods and Quality Assurance Plans;

- Providing an external and, thereby, independent QA review of our subcontracted laboratory activities and documentation (including all control charts and a 10 percent review of data packages and IRDMIS data files);

- Coordinating with USAEC, Arthur D. Little, and DataChem to ensure that QA objectives appropriate to the project are established and that DataChem personnel are aware of these objectives;

- Coordinating with DataChem management and personnel to ensure that QC procedures, appropriate to demonstrating data validity and sufficient to meet QA objectives, are developed and in place;

- Ensuring data are properly reviewed by an Arthur D. Little QA chemist, including resolving any discrepancies between DataChem and the validator;

- Requiring and/or reviewing corrective actions taken in the event of QC failures; and

- Reporting non-conformance with QC criteria or QA objectives, including an assessment of the impact of the data quality or project objectives, to the Program QA Officer and Task Manager.

2.3 DataChem Project QA/QC Organization

The DataChem Laboratory Organization is described in the DataChem QA Program Plan, Section 3, Organization and Responsibilities, provided in Appendix A.

Responsibilities of the DataChem Analytical Task Manager (James H. Nelson) include but are not limited to:

- Through the Arthur D. Little Task Manager, submit to Arthur D. Little for approval a detailed QAPjP specific to the USAEC project being supported;

- Support a Quality Assurance Coordinator (QAC) who will not be subordinate to or be in charge of any person having direct responsibility for sampling or analyses;

- Provide sufficient equipment, space, resources, and personnel to conduct analyses and implement the USAEC project and QA Program;

- Submit the required documentation and laboratory certification data to Arthur D. Little prior to analyzing field samples;

- Ensure that subsampling and other handling procedures in the laboratory are adequate for the sample types received;

- Oversee the quality of purchased laboratory materials, reagents, and chemicals to ensure that these supplies do not jeopardize the quality of analytical results; and

- Ensure implementation of corrective action for any QA/QC deficiencies.

The DataChem Quality Assurance Coordinator (Lance H. Eggen Berger) will:

- Monitor the QA and QC activities of the laboratory to ensure conformance with authorized policies, procedures, and sound practices, and recommend improvements as necessary;

- Inform the Arthur D. Little Task Manager, Arthur D. Little Lead Chemist, and laboratory management of nonconformance to the QA Program;

- Request analytical reference materials from USAEC through the USAEC Chemistry Branch;

- Ensure that all records, logs, standard procedures, project plans, and standing operating procedures are distributed to all laboratory personnel involved in the project;

- Establish, with the analysts and the Arthur D. Little Lead Chemist, the correct analytical lot size, the correct QC samples to be included in each lot, and the correct procedures for evaluating acceptable, in-control analytical performance;

- Ensure that logging of received samples includes establishing appropriate lot size for each analysis and allocating sample numbers for the correct control samples in each lot and that checklist is filled out and maintained;

- Review all laboratory data before those data are transmitted to permanent storage, reported to other project participants, or submitted via the USAEC Installation Restoration Data Management Information System (IRDMIS). Before data are released, the QAC must have completed the Contractor QAC Checklist (Appendix P) and inspected calibration data, control charts, and other performance indicators to verify that the data were collected under conditions consistent with laboratory certification and that the analytical systems were in control;

- Ensure that a signed Data Package Checklist is included in each completed data package;

- Ensure that analysts are preparing QC samples, maintaining control charts, and implementing and documenting corrective action when necessary;

- Ensure that all sampling logs, instrument logs, and QC documents are maintained and are completed with the required information;

- Collect control charts from analysts, discuss control chart results with the Analytical Task Manager, and submit the charts to Arthur D. Little and the USAEC Chemistry Branch on a weekly basis;

- Maintain an awareness of the entire laboratory operation to detect conditions which might directly or indirectly jeopardize controls of the various analytical systems (Examples: improper calibration of equipment; cross contamination through improper storage of samples); and

- Audit sampling documentation and procedures to ensure that samples are labeled, preserved, stored, and transported according to prescribed methods following approved chain-of-custody procedures.

3.0 QA Objectives for Measurement Data in Terms of Precision, Accuracy, Representativeness, Completeness, Comparability

3.1 Introduction

QA objectives are qualitative and quantitative statements which specify the quality of data necessary for regulatory and/or project specific decisions. The process of developing QA objectives for a given study helps to ensure that data generated are of adequate quality for the intended use. QA objectives are expressed in terms of precision, accuracy, representativeness, completeness, and comparability.

The objectives in this section generally apply to all Fort Devens investigations. Exceptions and/or additions for specific Delivery Orders are provided in the supplements to the QAPjP.

3.2 QA Objectives for Fort Devens Data

QA objectives for the data collected under the Fort Devens investigations covered by this QAPjP have been defined to ensure that the collected data will be of sufficient quality to support the decision-making needs of the USAEC program. In order to provide a common point of reference for all projects and ensure comparability of the data generated within the USAEC program, USAEC prescribes the use of standardized analytical methods which provide sufficient information to evaluate data quality. For specific methods, the *USATHAMA Quality Assurance Program* defines QA objectives through a process of method performance demonstration, including pre-performance demonstrated calibration and performance demonstrated analyses: the USAEC Chemistry Branch determines whether the results of these analyses demonstrate proficiency of the laboratory and, if proficiency is demonstrated, assigns method numbers to be used when reporting data. This effort also provides the baseline for establishing control limits for daily analyses. Where possible, USAEC-approved analytical methods will be used for the analysis of Fort Devens samples; for non-USAEC methods, analyses will be performed based on standard EPA methods.

An MRD validated laboratory, DataChem Laboratories, will be used to perform all analyses on the field samples collected at Fort Devens. DataChem Laboratories QA Program Plan for USAEC Laboratory Analyses is attached as Appendix A to this QAPjP. All analytical methods used for Fort Devens investigations will generate appropriate QC data to enable data quality to be assessed with respect to the QA objectives of the project.

USAEC analytical methods are characterized by rigorous QA/QC protocols and documentation requirements. USAEC data are of high quality, comparable to EPA Level IV data quality (Data Quality Objectives for Remedial Response Activities, USEPA, EPA/540/G-87/003, March 1987). The USAEC-approved methods that will be used for Fort Devens investigations are presented in Table 3-1. The methods for the specific Delivery Orders are provided in the supplements.

The Target Analyte List (TAL) of metals and Target Compound List (TCL) of volatile and semivolatile organics are defined by the U.S. Environmental Protection Agency (U.S. EPA) Contract Laboratory Program (CLP). The specific constituents analyzed as part of these multi-analyte methods, as well as the other multi-analyte methods, HPLC explosives and GC/ECD PCBs, are provided in Table 7-2.

There are also a number of non-USAEC methods that will be used during Fort Devens investigations and are presented in Table 3-2. These analyses will be performed using EPA or other published methods, with specified QA/QC requirements. The quality of the data generated using these methods is comparable to EPA Level III data quality (*Data Quality Objectives for Remedial Response Activities*, USEPA, EPA/540/G-87/003, March 1987).

In tasks where cases where the use of non-USAEC performance demonstrated laboratories are required, the Lead Chemist will review their QAP to ensure it meets the appropriate EPA and MDEP requirements. A field laboratory will also be installed at the site to obtain field screening measurements. This data will provide real-time data to assist in the optimization of the field sampling activities. The quality of the data generated at the field laboratory will be at Level II as defined by the EPA. We will use suitable calibration standards, reference materials, and sample preparation equipment to ensure meeting the quality objectives. Field screening measurements will also be collected using portable equipment to assist in the field effort and for health and safety purposes. Field measurements such as pH, temperature, conductivity, and volatile organics in air, (using a photoionization detector) will be obtained. The quality of these data is generally comparable to EPA Level I.

Tables 3-3 and 3-4 present the data quality objectives for critical measurements in terms of precision, accuracy, and completeness for all parameters analyzed for this investigation. The tables specify whether the measurement will be made in the field or in the laboratory. Estimated accuracy is expressed as percent recovery and estimated precision is expressed as a relative percent difference (for two values) or a standard deviation (for three or more values). Completeness is expressed in terms of the percentage of valid data generated out of the total number of data points. The information regarding precision and accuracy of the methods presented in this plan has been obtained from a number of sources. For the EPA methods used in this investigation, the precision and accuracy values come from a program for evaluating analytical methods and laboratories that is directed by the Environmental Protection Agency. For the USAEC-approved methods precision and accuracy are evaluated as part of the control chart program. All these indicators of data quality are explained in further detail in the sections that follow.

Table 3-1: USAEC Approved Methods used in the Analytical Program

ANALYSIS	METHOD[a]	TECHNIQUE
TCL Volatile Organic Compounds	USAEC	PAT/GC/MS
TCL Semivolatile Organic Compounds	USAEC	GC/MS
TCL Pesticides/PCBs	USAEC	GC/ECD
TCL PCBs	USAEC	GC/ECD
Organophosphorus Pesticides	USAEC*	GC/NPD
TAL Metals	USAEC	ICAP/GFAA
Herbicides	USAEC*	GC/ECD
Chloride/Sulfate	USAEC	Ion Chromatography
Total Kjeldahl Nitrogen	USAEC	Colorimetric
Total Phosphorus	USAEC	Colorimetric
Explosives	USAEC	HPLC

* = This method will include additional compounds not certified by USAEC to be determined by review of historical records.
a = USAEC-approved methods are referenced in Table 7-1.

Table 3-2: Non-USAEC Methods Used in the Analytical Program

ANALYSIS	METHOD[a]	TECHNIQUE
Phosphate	EPA 365.1	Colorimetric
Total Petroleum Hydrocarbons	EPA 418.1	Spectrophotometric, Infrared
Hardness	EPA 130.1	Colorimetric, automated EDTA
Alkalinity	EPA 310.2	Colorimetric
Total Suspended Solids	EPA 160.2	Gravimetric
Toxicity Characteristic Leaching Procedure (TCLP)	EPA 1311	Filtration
TCLP Volatile Organic Compounds	SW-846 8240	PAT/GC/MS
TCLP Semivolatile Organic Compounds	SW-846 8270	GC/MS
TCLP Pesticides/Herbicides	SW-846 8080/8150	GC/ECD
TCLP Metals	SW-846 6010/7000	GFAA/ICAP
Corrosivity	SW-846 1110	Corrosivity Toward Steel
Ignitability	SW-846 1010	Closed Cup
Reactivity	EPA OSW	Reactive CN, H_2S
Total Organic Carbon	EPA 415.1	Combustion
Grain size	ASTM 43-2	Sieve Gradient
Asbestos	NIOSH 9002	PLM

a = Method references are listed on Table 3-4.

Table 3-3: Data Quality Objectives for USAEC-Approved Methods: Precision, Accuracy, and Completeness

Lab/Field QC[a]	Parameter	Matrix	Estimated Accuracy[b,c]	Estimated Precision[b,c]	Field Duplicates RPD-DQO	Completeness
Lab USAEC	TCL VOAs	Soil/Sed	80-120%	≤20%	RPD ≤30%	90%
Lab USAEC	TCL SVOAs	Soil/Sed	60-140%	≤25%	RPD ≤30%	90%
Lab USAEC	TAL Metals	Soil/Sed	80-120%	≤20%	RPD ≤30%	90%
Lab USAEC	TCL Pesticides/PCBs	Soil/Sed	70-120%	≤25%	RPD ≤30%	90%
Lab USAEC	TCL PCBs	Soil/Sed	70-120%	≤20%	RPD ≤30%	90%
Lab USAEC	Organophosphorous Pesticides	Soil/Sed	70-120%	≤25%	RPD ≤30%	90%
Lab USAEC	HPLC Explosives	Soil/Sed	80-120%	≤20%	RPD ≤30%	90%
Lab USAEC	Nitrate	Soil/Sed	80-120%	≤20%	RPD ≤30%	90%
Lab USAEC	Sulfate	Soil/Sed	80-120%	≤20%	RPD ≤30%	90%
Lab USAEC	Herbicides	Soil/Sed	60-110%	≤25%	RPD ≤30%	90%
Lab USAEC	TCL VOAs	Aqueous	80-120%	≤20%	RPD ≤30%	90%
Lab USAEC	TCL SVOAs	Aqueous	60-140%	≤25%	RPD ≤30%	90%
Lab USAEC	TAL Metals	Aqueous	90-110%	≤10%	RPD ≤30%	90%
Lab USAEC	Chloride	Aqueous	90-110%	≤10%	RPD ≤30%	90%
Lab USAEC	Nitrate	Aqueous	90-110%	≤10%	RPD ≤30%	90%
Lab USAEC	Sulfate	Aqueous	90-110%	≤10%	RPD ≤30%	90%
Lab USAEC	Explosives	Aqueous	70-110%	≤20%	RPD ≤30%	90%
Lab USAEC	TCL Pesticides/PCBs	Aqueous	80-120%	≤20%	RPD ≤30%	90%
Lab USAEC	Organophosphorus Pesticides	Aqueous	80-120%	≤20%	RPD ≤30%	90%
Lab USAEC	Herbicides	Aqueous	60-110%	≤25%	RPD ≤30%	90%
Lab USAEC	Total Kjeldahl Nitrogen	Aqueous	90-110%	≤10%	RPD ≤30%	90%
Lab USAEC	Total Phosphorous	Aqueous	90-110%	≤10%	RPD ≤30%	90%

a. USATHAMA, Quality Assurance Program, January 1990
b. For these USAEC-approved methods, the precision and accuracy limits will be based on the historical control chart data of DataChem Laboratories.
c. Values represent an average for the analyte group. Individual analyte behavior can significantly impact precision and accuracy. Low spike quality control samples tend to exhibit poorer precision and accuracy.

RPD: Relative Percent Difference.

Table 3-4: Data Quality Objectives for Non-Approved Methods: Precision, Accuracy, and Completeness

Lab/Field QC	Parameter	Matrix	Estimated Accuracy[d]	Estimated Precision[d]	Completeness
Lab Non-USAEC[a]	Hydrocarbons	Soil/Sed	50 - 120%	RPD ≤75%[c]	90%
Field Non-USAEC[a]	pH	Aqueous	±0.2 pH units	±0.2 pH units[c]	90%
Field Non-USAEC[a]	Temperature	Aqueous	±1°C	±1°C[c]	90%
Field Non-USAEC[a]	Conductivity	Aqueous	±2% scale	±2% scale[c]	90%
Field Non-USAEC[a]	Turbidity	Aqueous	±2% scale	±2% scale[c]	90%
Lab Non-USAEC[b]	TCL Volatile Organics	TCLP Extract	75-125%	RPD ≤20%	90%
Lab Non-USAEC[b]	TCL Pesticides	TCLP Extract	70-120%	RPD ≤20%	90%
Lab Non-USAEC[b]	TCL Semivolatile Organics	TCLP Extract	60-140%	RPD ≤25%	90%
Lab Non-USAEC[b]	TCL Herbicides	TCLP Extract	60-110%	RPD ≤25%	90%
Lab Non-USAEC[b]	TAL Metals	TCLP Extract	±15%	RPD ≤10%	90%
Lab Non-USAEC	Phosphate	Aqueous	80-120%	RPD ≤20%	90%
Lab Non-USAEC	Phosphate	Soil/Sed	70-130%	RPD ≤20%	90%
Lab Non-USAEC	TPHC	Aqueous	60-120%	RPD ≤75%[c]	90%
Lab Non-USAEC	Hardness	Aqueous	80-120%	RPD ≤15%	90%
Lab Non-USAEC	Alkalinity	Aqueous	80-120%	RPD ≤15%	90%
Lab Non-USAEC	Total Organic Carbon	Soil/Sed.	80-120%	RPD ≤15%	90%
Lab Non-USAEC	Total Suspended Solids	Aqueous	80-120%	RPD ≤15%	90%

a. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983 and EPA Water Pollution Performance Evaluation Data
b. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, January 1990
c. RPD-DQO is for the analysis of field duplicates.
d. See Method 1311 from *Test Methods for Evaluating Solid Waste Physical/Chemical Methods*, SW-846, 3rd Edition, January 1990.

3.2.1 Precision

Precision is the degree of mutual agreement among individual measurements of the same parameter, using prescribed conditions and a single test procedure. Overall precision includes variability associated with field and laboratory operations. The results of analyzing field duplicate samples are used to assess field variability, which is a function sample collection/handling as well as matrix homogeneity. Analytical precision can be express in several ways, including standard deviation, relative standard deviation, range, and relative percent difference (RPD).

- For the USAEC-approved methods, laboratory precision is evaluated as part of the control chart program. A three-day moving average control chart is maintained for each control analyte by plotting the range of recovery of spiked QC samples; an updated three-day average range of recovery for each compound is plotted on the control chart as part of the daily laboratory control program. This procedure is intended to monitor variations in the precision of routine analyses and detect trends in observed variations.

- For non-USAEC methods, laboratory precision is generally assessed through the use of laboratory duplicate samples or as specified in the method.

3.2.2 Accuracy

Accuracy is the difference between individual analytical measurements and the true or expected value of a measured parameter. It is a measure of the bias corresponding to systematic and random errors in the entire data collection process. Sources of error include the sampling process, field and laboratory contamination, sample preservation and handling, sample matrix interferences, sample preparation methods, and calibration and analysis procedures. Sampling accuracy can be assessed, in part, by evaluating the results of analyzing field/trip blanks; analytical accuracy can be evaluated through the use of calibration and method blanks, calibration verification samples, laboratory control samples, and matrix spikes.

- For the USAEC-approved methods, accuracy is assessed as part of the control chart program. A three-day moving average control chart is maintained for each control analyte by plotting the recovery of spiked QC samples; an updated three-day average recovery for each compound is plotted on the control chart as part of the daily laboratory control program. This procedure is intended to monitor variations in the accuracy of routine analyses and detect trends in the observed variations.

- For non-USAEC methods, laboratory accuracy is generally assessed through the use of laboratory spiked samples or as specified in the method.

3.2.3 Representativeness

Representativeness is the degree to which data accurately and precisely represent a characteristic of a population, parameter variation at a sampling point, or an environmental condition. A representative sample should possess the same qualities or properties relevant to the investigation as the material under investigation. Representativeness reflects the design of the sampling program; representativeness is maximized by proper selection of sampling locations and collection of a sufficient number of samples. Sampling locations for the Fort Devens investigations generally use a targeted sampling design. Areas of concern are selected to address data gaps from previous investigations; sampling locations are identified based on existing information and field survey data. Parameter variations at a sampling point can be evaluated on the basis of field duplicate results. Any exceptions to this general approach will be noted in the Delivery Order Specific supplements.

3.2.4 Completeness

Completeness is defined as the a measure of the amount (%) of valid data obtained from a measurement system, either field or laboratory, compared to the amount expected from the system. Completeness will be assessed in terms of the actual number and type of sample results received from the laboratory as compared with the planned number and type of results. A target of 90 percent completeness for all field and laboratory data is expected for Fort Devens investigations. Exceptions will be noted in the Delivery Order Specific supplements.

3.2.5 Comparability

Comparability addresses the confidence with which one data set can be compared to another. Use of appropriate sampling methods, chain-of-custody procedures, and USAEC-approved and EPA-approved analytical methods, as well as adherence to strict QA/QC procedures, provide the basis for uniformity in sample collection and analysis activities.

For the Fort Devens investigations, data will be considered valid with respect to the comparability objectives if the USAEC acceptance criteria for precision, accuracy, and any other method-specified quality criteria are achieved. Work is being conducted under the USAEC requirements for field sampling activities and laboratory analysis. To the extent possible, USAEC-approved methods are being used in a MRD validated laboratory. For non-USAEC analyses, USAEC requirements have been followed for using standardized methods with appropriate QA/QC protocols to generate data of known quality.

In addition, comparability is assured through the consistent use of units. The data collected as part of this program will be entered into IRDMIS in the units presented in Table 3-5.

Table 3-5: Analytical Program Reporting Units for IRDMIS

Parameter	Water	Soil/Sed	Wipe	Concrete
TCL Volatiles	µg/L	µg/g	NA	µg/g
TCL Semivolatiles	µg/L	µg/g	NA	µg/g
TCL Pesticides/PCBs	µg/L	µg/g	NA	µg/g
TCL Pesticides	µg/L	µg/g	$\mu g/cm^2$	NA
TCL PCBs	NA	µg/g	NA	µg/g
TAL Metals	µg/L	µg/g	NA	µg/g
Organophosphorus Pesticides	µg/L	µg/g	$\mu g/cm^2$	NA
Herbicides	µg/L	µg/g	$\mu g/cm^2$	NA
Total Petroleum Hydrocarbons	µg/L	µg/g	NA	NA
HPLC Explosives	µg/L	µg/g	NA	NA
IC Chloride, Sulfate, Nitrate/Nitrite	µg/L	µg/g	NA	NA
Total Suspended Solids	µg/L	NA	NA	NA
Phosphate	µg/L	µg/g	NA	NA
Total Organic Carbon	NA	µg/g	NA	NA
Total Phosphorus	µg/L	NA	NA	NA
Hardness	µg/L	NA	NA	NA
Total Kjeldahl Nitrogen	µg/L	NA	NA	NA
Alkalinity	µg/L	NA	NA	NA
Grain Size	NA	cm	NA	NA
Asbestos	NA	fiber/cm	NA	NA
pH	pH units	pH units	NA	NA
Temperature	°C	NA	NA	NA
Conductivity	$\mu mhos/cm^2$	NA	NA	NA
Turbidity	NTU	NA	NA	NA

NA = Not Applicable

4.0 Sample Collection

The quality of the data collected for Fort Devens investigations is a function of the overall design and planning for the sample collection program and the specific sample collection and handling procedures employed. In addition to the collection of samples, activities included within the sample collection and handling phase of field investigations includes preparation of sample containers, sample preservation, sample identification, sample handling and shipment, and chain-of-custody documentation.

The sampling programs for Fort Devens investigations are described in the Work Plans, provided as a separate documents. The Work Plans include documentation of the following aspects of the field investigation for each study area included in an investigation:

- Sampling Objectives and Rationale;
- Sample Location and Frequency; and
- Sample Designation.

Chemical analysis sampling summaries for specific Delivery Orders are provided in the supplements. In order to ensure that collected field samples are representative of the matrices under investigation and to ensure that the physical and chemical integrity of the samples is maintained prior to analysis in the subcontracted laboratory, detailed procedures for all aspects of sample collection and handling have been specified. These procedures comply with USAEC and U.S. EPA specifications and guidelines for the collection of environmental samples. A list of the Standard Operating Procedures (SOPs) that will be followed by the Arthur D. Little sampling staff is provided in Table 4-1. Any additional SOPs specific to a Delivery Order will be noted in the Delivery Order Specific supplements. The following sections of the QAPjP summarize these procedures for each element of the field investigation and are organized as follows:

Section 4.1 Sample Containers, Preservation, and Handling;
Section 4.2 Field QC Samples;
Section 4.3 Sample Handling; and
Section 4.4 Sampling Equipment and Procedures.

Table 4-1: List of Field and Laboratory SOPs

USATHAMA SOP Requirement	Arthur D. Little SOP Title	Document Control Number
Training	Training of Field Personnel	Pending
Sample Management	Sample Receipt and Log-in	ADL-1002
Numbering and Labeling	Management of USATHAMA Samples	USA-6003
Sample Tracking	Sample Custody	ADL-1001
Sample Containers	Sample Containers, Preservatives and Holding Times	USA-1000
Sample Preservation and Storage	Sample Containers, Preservatives and Holding Times Sample and Extract Storage	USA-1000 ADL-1005
Holding Times	Sample Containers, Preservatives and Holding Times	USA-1000
Shipping	Sample Custody	ADL-1001
Decontamination	Field Decontamination Sampling Equipment	USA-1008
Sample Collection Procedures	Wipe Sampling Sediment Sampling Concrete/Asphalt Chip Sampling Surface Water Sampling Standard Penetration Test and Split Spoon Sampling Ground Water Monitoring Well Sampling Exploratory Pit/Trench Procedures	ADL-1023 ADL-1024 ADL-1025 USA-1001 USA-4002 USA-1011 ADL-4000
Corrective Action	Corrective Actions for Field Operations	Pending
Records Management	Geotechnical Documentation	ADL-4014
Chemical and Sample Disposal	Chemical and Sample Disposal	Pending
Reporting	Geotechnical Documentation	ADL-4014

Table 4-1: List of Field and Laboratory SOPs (continued)

USATHAMA SOP Requirement	Arthur D. Little SOP Title	Document Control Number
Records Management	Geotechnical Documentation	ADL-4014
Chemical and Sample Disposal	Chemical and Sample Disposal	USA-3000
Reporting	Geotechnical Documentation	ADL-4014
Field Analyses	Conductivity Meter Calibration and Measurement pH Meter Operation Inspection and Use of the MSA 261 Combustible gas/Oxygen Meter	ADL-5011 ADL-5013 ADL-5018
Geotechnical*	Exploratory Boring Procedures	USA-4001
Geotechnical*	Standard Penetration Tests and Split Spoon Sampling	USA-4002
Geotechnical*	Grouts Methods and Criteria	USA-4003
Geotechnical*	Monitoring Well Development	USA-4010
Geotechnical*	Monitoring Well Water Level Measurement Procedure	USA-4012
Geotechnical*	In-Situ Permeability Testing (Slug Testing) with Hydraulic Conductivity Data Reduction	ADL-4018

* Arthur D. Little requirement, not a USATHAMA requirement

Table 4-1: List of Field and Laboratory SOPs (continued)

USATHAMA SOP Requirement	DataChem SOP Title	Document Control Number
Sample receipt and log-in	Sample Receipt and Logging Chain-of-Custody and Laboratory Tracking	SOP-EPA-100 SOP-EPA-1210
Laboratory personnel training	Record of Training	SOP-GLP-007
Sample storage	Security of Laboratory Samples	SOP-EPA-400
Sample scheduling	Chain-of-Custody and Laboratory Tracking	SOP-EPA-1210
Preventing sample contamination	Preventing Sample Contamination	SOP-EPA-300
Security for laboratory, samples and standards	Security of Laboratory Samples	SOP-EPA-400
Traceability/Equivalency of standards	Standards Purity, Traceability and Verification	SOP-EPA-500
Standard solution verification	Standards Purity, Traceability and Verification	SOP-EPA-500
Maintaining instruments records an logbooks	Documentation - Maintaining Instrument Records, Notebooks and Logbooks	SOP-EPA-600
Sample analysis and data control systems	Data Control Systems - Calibration	SOP-EPA-700
Glassware cleaning	Glassware Cleaning - Organic Analysis Glassware Cleaning - Inorganic Analysis	SOP-EPA-810 SOP-EPA-820
Technical and managerial review of laboratory operation and data package preparation	Technical and managerial review of laboratory operation and data package preparation	SOP-EPA-900
Internal review of contractually-required quality assurance and quality control data for each individual data and reporting	Internal Review of QA/QC Data Document Control and Report Preparation	SOP-EPA-1000 SOP-EPA-1220
Data reduction and validation	Sample Data Validation/Self-Inspection System	SOP-EPA-1300

4.1 Sample Containers, Preservation, and Handling

4.1.1 Sample Containers

To ensure the integrity of the field samples, specific steps must be taken to minimize the potential for contamination from the containers in which the samples are stored. Sample containers must be compatible with the analytes of interest. The following general recommendations will be followed: septum-sealed amber glass vial for volatile compounds; amber glass bottles with Teflon-lined lids for organic compounds other than volatiles; polyethylene bottles for inorganic analytes; and wide-mouth amber glass bottles for all soil and sediment samples. The sample containers which could be required for the collection of the various analytical samples for Fort Devens investigations are indicated in Table 4-2.

For Fort Devens investigations, all sample containers will be supplied by the subcontracted laboratory. All sample containers will be cleaned prior to shipment to the field. Cleaning procedures will be applied to new containers; reuse of sample containers is expressly prohibited. The cleaning procedures used by the laboratory are described in the appropriate SOP provided in Appendix B to this plan. These procedures meet the specifications of the sample container cleaning procedures outlined in the *USATHAMA Quality Assurance Program.*

4.1.2 Sample Preservation and Holding Times

The purpose of sample preservation is to prevent or retard the degradation or transformation of target analytes in the field samples during transport and storage. Preservation efforts to ensure sample integrity will be initiated at the time of sampling and will continue until the analyses are performed. Preservatives will be added to the sample container at the time of sample collection. The preservatives which could be required for specific analytical samples to be collected for the Fort Devens investigations are indicated in Table 4-2.

Chemical preservatives will be supplied to the field by the analytical laboratory subcontracted for these investigations. Bottles for aqueous samples will be triple-rinsed with the water being sampled, according to USAEC requirements, before the addition of preservatives. For volatiles analyses, the preservative will be added before sample container is filled; for all other analyses, the sample container will be filled and then the preservative will be added. For surface water samples, preservatives will be added to the volatiles container after sample collection, if the container is used as the sample collection device.

After collection and preservation, all samples will be stored and shipped at 4 degrees Celsius. Samples will be sent to the laboratory for analysis as expeditiously as possible to ensure data quality. The recommended maximum holding times for

Table 4-2: Containers, Preservation, and Holding Times for Analytical Samples

Analysis-Media	Sample Containers[1]	Preservation	Holding Times
TCL Volatiles - water	Two 40-mL amber glass VOA vials, Teflon-lined cap	HCl to pH<2 Cool, 4°C	14 days
TCL Volatiles - soil/sediment/ concrete chips	250-mL amber wide-mouth glass jar, Teflon-lined cap	Cool, 4°C	14 days
TCL Semivolatiles - water	1-L amber glass bottle, Teflon-lined cap	Cool, 4°C	7 days to extraction; 40 days after extraction
TCL Semivolatiles - soil/sediment/ concrete chips	250-mL amber wide-mouth glass jar, Teflon-lined cap [a]	Cool, 4°C	7 days to extraction; 40 days after extraction
TCL Pesticides/PCBs - water	1-L amber glass bottle Teflon-lined cap	Cool, 4°C	7 days to extraction; 40 days after extraction
TCL Pesticides/PCBs - soil/sediment/ concrete chips	250-mL amber wide-mouth glass jar, Teflon-lined cap [a]	Cool, 4°C	7 days to extraction; 40 days after extraction
TCL PCBs - soil/sediment	250-mL amber wide-mouth glass jar, Teflon-lined cap [a]	Cool, 4°C	7 days to extraction; 40 days after extraction
Organophosphorus Pesticides - soil/sediment	250-mL amber wide-mouth glass jar, Teflon-lined cap [a]	Cool, 4°C	7 days to extraction; 40 days after extraction

Table 4-2: Containers, Preservation, and Holding Times for Analytical Samples (continued)

Analysis-Media	Sample Containers[1]	Preservation	Holding Times
Organophosphorus Pesticides - water	1-L amber glass bottle Teflon-lined cap	Cool, 4°C	7 days to extraction; 40 days after extraction
Explosives - soil/sediment	250-mL amber wide-mouth glass jar, Teflon-lined cap	Cool, 4°C	7 days to extraction; 40 days after extraction*
TAL Metals (ICP/GFAA) - water	1-L Polyethylene bottle, Teflon-lined cap	HNO_3 to pH<2	6 months
TAL Metals (ICP/GFAA) - soil/sediment/ concrete chips	250-mL amber wide-mouth glass jar, Teflon-lined cap [b]	Cool, 4°C	6 months
Mercury - water	1-L polyethylene bottle, Teflon-lined cap	HNO_3 to pH<2	28 days
Mercury - soil/sediment	250-mL amber wide-mouth glass jar, Teflon-lined cap	Cool, 4°C	28 days
Chloride/Sulfate - water	250-mL polyethylene bottle [c]	Cool, 4°C	28 days
Chloride/Sulfate - soil/sediment	250-mL amber wide-mouth glass jar	Cool, 4°C	28 days
Nitrate plus Nitrite - water	250-mL polyethylene bottle [d]	H_2SO_4 to pH<2 Cool, 4°C	28 days
Nitrate plus Nitrite - soil/sediment	250-mL amber wide-mouth glass jar [b]	Cool, 4°C	28 days

Table 4-2: Containers, Preservation, and Holding Times for Analytical Samples (continued)

Analysis-Media	Sample Containers[1]	Preservation	Holding Times
Total Suspended Solids (TSS) - water	250-mL polyethylene bottle [c]	Cool, 4°C	7 days
Total Petroleum Hydrocarbons (TPHC) - soil/sediment	250-mL amber wide-mouth glass jar, Teflon-lined cap	Cool, 4°C	28 days
Total Petroleum Hydrocarbons (TPHC) - water	Two 1-L amber glass bottles w/Teflon-lined caps	Cool, 4°C	28 days
TCLP Analytes Organics & Inorganics (volatiles, semi-volatiles, pesticides, herbicides, and metals) - water	1-L clear bottle with Teflon-lined cap and Two 4-L amber glass bottles, Teflon-lined cap	Cool, 4°C	**
TCLP Analytes (volatiles, semi-volatiles, pesticides, herbicides, and metals) - soil/sediment	Two 250-mL amber wide-mouth glass jars, Teflon-lined cap	Cool, 4°C	**
Herbicides - soil/sediment	250-mL amber wide-mouth glass jar, Teflon-lined cap [a]	Cool, 4°C	7 days to extraction; 40 days after extraction
Herbicides - water	1-L amber glass bottle Teflon-lined cap	Cool, 4°C	7 days to extraction; 40 days after extraction
TCL Pesticides/PCBs - water	1-L amber glass bottle Teflon-lined cap	Cool, 4°C	7 days to extraction; 40 days after extraction

Table 4-2: Containers, Preservation, and Holding Times for Analytical Samples (continued)

Analysis-Media	Sample Containers[1]	Preservation	Holding Times
Explosives - water	1-L amber glass bottle Teflon-lined cap	Cool, 4°C	7 days to extraction; 40 days after extraction
Total Organic Carbon (TOC) - soil - water	250-mL amber wide-mouth glass jar, Teflon-lined cap	Cool, 4°C	28 days
TKN - water	1-L polyethylene bottle, Teflon-lined cap [d]	H_2SO_4 to pH<2 Cool, 4°C	28 days
Total Phosphorus - water	250-mL polyethylene bottle [d]	H_2SO_4 to pH<2 Cool, 4°C	28 days
Phosphate - water	250-mL polyethylene bottle [c]	Cool, 4°C	48 hours
Phosphate - soil	250-mL amber wide-mouth glass jar [b]	Cool, 4°C	48 hours
Hardness - water	100-mL polyethylene bottle, Teflon-lined cap [c]	H_2SO_4 to pH<2 Cool, 4°C	6 months
Alkalinity - water	250-mL polyethylene bottle, Teflon-lined cap [c]	Cool, 4°C	14 days
Total Suspended Solids (TSS) - water	250-mL polyethylene bottle [c]	Cool, 4°C	7 days
Asbestos - soil	250-mL amber wide-mouth glass jar	Cool, 4°C	NA

Table 4-2: Containers, Preservation, and Holding Times for Analytical Samples (continued)

Analysis-Media	Sample Containers[1]	Preservation	Holding Times
Grain Size	250-mL amber wide-mouth glass jar	NA	NA
TCL Pesticides - wipes	250-mL amber wide-mouth glass jar	Cool, 4°C	7 days to extraction; 40 days after extraction
Herbicides - wipes	250-mL amber wide-mouth glass jar	Cool, 4°C	7 days to extraction; 40 days after extraction
Organophosphorus Pesticides - wipes	250-mL amber wide-mouth glass jars	Cool, 4°C	7 days to extraction; 40 days after extraction

* The holding times for the Explosives analysis are specified in the *USATHAMA Quality Assurance Program* based on the results of a study by Oak Ridge National Laboratory.

** The analytical holding times for the TCLP samples are provided on the following page.

1) The designations a through d in the sample container column indicate groups of analytes which can be combined in the same sample container.

Table 4-2: Containers, Preservation, and Holding Times for Analytical Samples (continued)

TCLP Analysis	Max. Time: Sampling to TCLP Extraction	Max. Time: TCLP Extraction to Sample Prep.	Max. Time: Sample Prep. to Analysis	Max. Total Elapsed Time from Sample Collection
Volatiles	14 days	-	14 days	28 days
Semi-volatiles/ Pesticides/PCBs/ Herbicides	7 days	7 days	40 days	54 days
Metals	180 days	-	180 days	360 days
Mercury	28 days	-	28 days	56 days

Source: USATHAMA Quality Assurance Program (January 1990). TCLP information was taken from 40 CFR 261.

analytical samples are indicated in Table 4-2; maximum holding times are calculated from the date of sample collection. The indicated holding times will be adhered to by the laboratory subcontracted for analysis of samples. Freezing of samples to extend the holding time is not permitted.

4.2 Field QC Samples

The frequency of field QC samples is summarized in Table 4-3. The type of field QC samples to be collected as part of the specific Delivery Orders are provided in the supplements. The purpose of the various types of QC samples is summarized below:

- Field Blanks - The results of analyzing field blanks are used to check the cleanliness and effectiveness of field handling methods;
- Trip Blanks - The results of analyzing trip blanks are used to assess potential contamination during sample transport;
- Equipment/Rinsate Blanks - The results of analyzing equipment/rinsate blanks are used to evaluate potential cross-contamination from field sampling equipment; and
- Field Duplicates/Collocates - The results of analyzing field duplicates/collocates are used for assessing the consistency of the field and analytical program.
- Matrix Spike/Matrix Spike Duplicates - The results of matrix spike/matrix spike duplicate samples will be used to determine the precision and accuracy of the laboratory methods.

The field QC samples will be treated by the laboratory in the same manner as field samples. The purpose of the field QC samples and the frequency of collection are further discussed in Section 9.2 of this QAPjP.

4.3 Sample Handling

All samples, including field QC samples, will be maintained in a manner which assures the integrity and representativeness of each sample from the time of collection to laboratory analysis. This maintenance includes the accurate completion of all required documents and the secure packaging of samples prior to transport and shipment. Secure packaging includes the following steps.

Table 4-3: Frequency of Field Quality Control Samples

Field Blank:	One per 20 samples or 5%, whichever is greater[a]; ASTM Type I deionized water or equivalent used for organic field blanks; distilled, deionized water used for inorganic field blanks.
Equipment/ Rinsate Blank:	One per day per equipment type; ASTM Type I deionized water or equivalent used for organic rinsate blanks; distilled, deionized water used for inorganic rinsate blanks.
Trip Blank:	For volatile organic analyses; minimum is one per cooler containing any samples for volatile organic analyses. Purged deionized ASTM Type I deionized water or equivalent is to be used for trip blanks.
Field Duplicate:	One per 20 samples or 5%[a] per matrix.
Matrix Spike/ Matrix Spike Duplicate:	Organic analysis only: one set per matrix per area, but no more than one set per 20 samples or 5%[a]; actual field sample must be used.[b]
Matrix Spike/ Lab Duplicate:	Inorganic analysis only; one set per matrix per area, but no more than one set per 20 samples; actual field sample must be used.

a = When a group of less than 20 samples is collected during a sampling event, blanks, duplicates, and MS/MSD samples need to be collected, resulting in a higher percentage of QA/QC samples than indicated above.

b = Additional sample volume may be required.

- Each sample label is individually wrapped in clear tape to protect the label from water damage, and to assure the sample label is not detached from the sample;
- Each sample bottle will be individually wrapped in bubblewrap to reduce the potential for breakage during transport;
- All samples associated with a shipment will be placed in a rigid pre-cooled container with ample coolant to maintain the samples at 4°C during transport and shipping;
- Individual cooler packing lists and chain-of-custody forms will be placed inside the coolers and will accompany each sample shipment;
- Any open space remaining in the cooler(s) will be filled with bubblewrap to eliminate motion within the cooler;
- Each packed cooler will have a signed and dated custody seal placed across the opening to insure that the cooler will not be opened until it reaches the laboratory;
- Each cooler custody seal will be protected with clear tape to insure its integrity during transport and shipping; and
- The individual shipping numbers will be maintained in a field notebook in case tracking of the shipment is required.

4.4 Sampling Equipment and Procedures

The various sampling and data collection procedures which will be followed are presented below, and include discussions of the various sampling and data acquisition equipment which will be used for each activity. The sample collection techniques are based on the guidelines in the USAEC Quality Assurance Program (QAP) and the USAEC Geotechnical Requirements for Drilling, Monitor Wells, Data Acquisition, and Reports. All standard operating procedures referenced in this section are listed in Table 4-1 and included as Appendix D in Volume II of the QAPjP.

4.4.1 Test Pit Sampling Procedures

Soil samples from the various exploratory test pit excavations will be collected in accordance with the procedures defined in Standard Operating Procedure (SOP) ADL-4000. In general, these procedures include the following:

- Heavy equipment (eg. backhoes, trailers, pumps, compressors, generators etc.) will be inspected by the Site Geologist. This inspection will evaluate the condition of the equipment with respect to potential contamination sources. No equipment which is observed to be leaking or saturated with petroleum products, hydraulic fluid, transmission fluid, or coolant will be utilized on site until the source of the contaminants has been identified and addressed, and the contamination has been removed via steam cleaning (SOP ADL-4007) and approved by Arthur D. Little, Inc. Equipment will be cleaned between test pits by steam cleaning.

- Knowledgeable parties (eg. public utility companies, plant engineers etc.) must approve the pit or trench location to assure risk minimization with respect to encountering unexpected subsurface hazards and obstacles. In cases where information on subsurface conditions is limited, subsurface clearance may require confirmation using geophysical techniques to assure safety.

- Using a compass and tape measure, the Site Geologist shall locate the center of each pit and/or the end points of each trench with respect to a permanent fixed marker (e.g., property corners). Additionally the orientation of each pit and trench shall also be identified with a wooded stake.

- Excavation procedures will include the establishment of a work zone using Caution/Hazard tape. The soils will be deposited in a manner which minimizes the potential for a "cave-in" and will be regularly monitored for volatile organic compounds. All readings are to be recorded in the field note book and appropriate geotechnical forms along with the approximate depth from which the soil pertaining to specific readings was excavated.

- Construction of each pit or trench will comply with OSHA regulations as described in 29 CFR 1926. Unless otherwise specified, all chemical and geotechnical soils samples will be collected as composites from the spoils pile. <u>At no time is anyone to enter the exploratory pit or trench</u>.

- Identify and log one wall of the pit or trench including a schematic wall diagram, upon completion of the excavation. Additionally, the geologist shall determine the pit or trench dimensions, depth to water, and photodocument the logged wall using a stadia rod or equivalent for scale.

- Upon completion of each exploratory pit or trench, excavated materials will be immediately and completely returned to the excavation, and tamped flush with the ground surface.

- If equipment failure occurs on site, which results in the release of any hazardous material (eg. petroleum products, hydraulic fluids, transmission fluids etc.), the source will be immediately isolated and contained, and precautionary measures (eg. lined with plastic etc.) will be taken to protect the site from contamination.

- Documentation of pit and trenching activities including geotechnical forms and the maintenance of a detailed field notebook are described in SOP ADL-4014.

4.4.2 Surface Water Sampling Procedures

Surface water samples will be collected in conformance with the procedures set forth in Section C.3.3.1.3 of the USAEC TEPS Contract DAA15-90-R-0120 and SOP USA-1001 as follows:

- All equipment used to collect samples will be cleaned prior to use and between sample collection in accordance with SOP USA-1008;

- Surface water samples will be collected from streams, rivers and standing water bodies during periods of moderate flow. Precipitation records for the week prior to sampling will be maintained to confirm the relative flow state;

- The surface water column will be measured and recorded using a weighted tape. The position of the sampling point to the shoreline will also be measured and recorded. Records will include detailed sketches of each sample location for future reference. Each location will also be plotted on the detailed site basemap;

- Continuous vertical profile temperature measurements will be collected at surface water sampling locations where the depth of water is greater than four feet to determine the presence of a thermocline. If a thermocline is present, surface water samples will be collected both above and below the thermocline depth for chemical analyses using a decontaminated stainless steel discrete bomb sampler;

- Samples from ditches, streams, and wetlands will be taken at approximately one half to two thirds of the water depth using a decontaminated stainless steel discrete bomb sampler. In cases where the depth to water is less than one foot, samples will be collected by direct submergence of the sample containers;

- The pH, temperature, specific conductivity, and turbidity of each surface water sample will be measured immediately prior to collection;

- All sample containers and lids will be triple rinsed with the sampled surface water prior to filling;

- Preservatives will be added to the sample following rinsing, as indicated on Table 4-3 and in Subsection 4.2.2;

- Preservatives will be added following sample collection if the containers are used as the sample collection device; and

- Sample collection will proceed from downstream to upstream locations to minimize disturbance of downstream locations.

4.4.3 Sediment Sampling Procedures

Each sediment sample will be collected in accordance with SOP ADL-1024 as summarized below:

- All equipment used to collect samples will be cleaned before use and between samples in accordance with SOP USA-1008;

- The surface water column above each sediment sampling location will be measured and recorded using a weighted tape. The position of the sampling point to the shoreline will also be measured and recorded. Records will include detailed sketches of each sample location for future reference. Each location will also be plotted on the detailed site basemap;

- For sediment collection below relatively shallow surface water bodies (i.e., less than four feet deep) the sampling location will be accessed by the sampler from the downstream direction to minimize disruption of bottom sediment in the sample area. The sampler will be wearing chest waders and will be accompanied by a co-worker who will observe activities from shore in case of emergency and will document all sampling activities;

- For sediment collection below relatively deep surface water bodies (i.e., greater than four feet deep) the sampling location will be accessed by boat with a two-person crew (one to maintain position and document activities and one to perform sample collection);

- Samples will be collected using either a decontaminated stainless steel hand auger or a weighted stainless steel dredge; and

- Sample collection will proceed from downstream to upstream locations and surface water samples will be collected prior to sediment samples at the same location.

- Samples must contain greater than 30 percent solids in order to be considered valid.

4.4.4 Surface Soil Sampling Procedures

Surface soil samples will be collected by Arthur D. Little personnel using a decontaminated stainless steel hand auger. The hand auger will be rinsed with distilled water prior to collection of each sample designated for chemical analyses in accordance with SOP USA-1008. Soil samples will be collected as follows:

- Prior to initiating the hand auger sampling activities, a sheet of plastic will be placed adjacent to the sample location for temporary storage of all excavated soils during sampling;

- Locations will be cleared of surface debris and vegetation to expose fresh soil. In cases where the ground surface is grassy, an eight by eight inch square section of sod will be removed and set aside for later post-sampling replacement;

- The soil collected from a particular sampling interval is composited in a stainless steel bowl prior to distribution into the various chemical sample jars. However, if a sample is scheduled for volatile organic compound analysis, the appropriate sample bottle is filled using a representative portion of soil prior to compositing; and

- Completion of sampling activities will include the return of auger spoils to the borehole, the replacement of the sod patches, and the placement of a four foot long wooden stake painted fluorescent orange and marked with the sample point code number for future reference.

Documentation of these procedures will be maintained in a dedicated field notebook and on appropriate field sampling forms in accordance with SOP ADL-4014. Records will include detailed sketches of each sample location for future reference, and each location will also be plotted on the detailed site basemap.

4.4.5 Concrete/Asphalt Chip Sampling Procedures

Each concrete chip and asphalt sample will be collected in accordance with SOP ADL-1025 as summarized below:

- All equipment used to collect samples will be cleaned before use and between samples in accordance with SOP USA-1008;

- Prior to collection of concrete chip samples, document the condition of the sample surface (i.e., note whether the surface is etched, weathered, cracked, painted, or stained);

- Establish a representative sampling grid throughout the entire area subject to potential spills, being sure to include etched stained areas if present;

- Each concrete chip and asphalt sample will be collected using a decontaminated hammer and chisel;

- The sample depth is determined by the intent of sampling (i.e., spill assessment or disposal characterization). To evaluate the potential for spills to have occurred or the effectiveness of clean up activities, the samples will be collected to reflect the surface (upper 1/8 inch). For disposal characterization, core samples will be collected;

- The volume of sample to be collected is determined by the analytical laboratory and depends on the coarseness of the concrete and the number of chemical parameters to be analyzed. Once the sample volume has been determined, the consistency of the sample volumes from location to location will be assured in the field using a balance; and

- The location of each sample will be documented in a dedicated field notebook and marked in the field with a surveyors PK nail and flagging for future reference.

4.4.6 Soil Boring Procedures

Each exploratory boring will be advanced in accordance with SOP USA-4001, using a truck-mounted hydraulic hollow stem auger drill rig which has the capability of converting to a drive and wash drilling method, as necessary.

All drilling supplies will be maintained by the drilling subcontractor. These supplies are likely to include extra hollow stem augers, steel casing, and grout.

Each drill rig and all drilling equipment such as hollow stem augers, steel casing, drill rods, mud tubs, and split spoon samplers will be steam cleaned immediately prior to initiation of drilling activities and between boring locations. The drilling subcontractor will supply steam cleaners and water trucks (as necessary). Drill water will be obtained from a tested and approved location.

Decontamination of all sampling equipment will be conducted prior to each use in accordance with SOP USA-1008. Each drill rig and all drilling equipment will be decontaminated prior to arrival on site, prior to relocation on site, and prior to leaving the site as specified in SOP ADL-4001. Drill rig and drilling equipment will be decontaminated in an area designated for this activity by the Base Commander through the USAEC Project Officer.

Split spoon sampling procedures will be performed in accordance with SOP USA-4002. Each exploratory boring will be abandoned in accordance with SOP USA-4003.

4.4.6.1 Subsurface Clearance Program. The final location of each surface soil sample and exploratory borehole will be determined prior to drilling and during the pre-drilling site visit. The soil boring locations will be cleared for underground utilities and obstructions through the review of utility records available at the base and through a Ground Penetrating Radar (GPR) Survey. The soil boring locations at areas where there is a potential for unexploded ordnance will also be cleared for unexploded ordnance (UXO) by a qualified subcontractor. UXO clearance will be performed at the surface prior to drilling and at four foot intervals during completion of the borings. The procedures for UXO clearance are provided in the UXO Subcontractor's procedures for Clearing Borings and Monitoring Well Locations, included as an Appendix to the Main Post SI Health and Safety Plan.

4.4.7 Ground Water Sampling Procedures

Ground water samples will be collected in accordance with SOP USA-1011.

The depth to water, total well depth, and thickness of any free-phase product which may be present within a well will be measured and recorded in accordance with SOP ADL-4012 prior to ground water sampling. A total of five purge volumes will be removed from each well immediately prior to sampling. The purge volume for each well includes the volume of standing water in the well plus the volume of water in the annular space surrounding the well over the same height. The volume of water within the annular space assumes 30 percent porosity.

During purging, the following aquifer stabilization parameters will be measured and recorded: pH, temperature, specific conductivity, and turbidity. Purging will continue until five well volumes are removed and parameters are stabilized to within approximately 10 percent. A minimum of three measurements will be recorded: 1) immediately upon initiation, 2) midway through purging, and 3) at completion of purging. All purging and sampling procedures will be conducted using a decontaminated, chemically inert, variable flow, submersible pump. However dedicated teflon bailers will be used to collect samples intended for volatile organic analyses. All sample bottles and lids will be triple rinsed with the well water prior to

filling. Each sample which requires filtering will be collected by attaching an in-line, 0.45 micron, disposable filter to the pump outflow. A new filter will be used at each sampling location. All samples will be preserved in the field as indicated in Table 4-3 of this plan.

An additional sample should be collected to test the pH. The pH of aqueous samples should be adjusted to less than two by carefully adding 1:1 HCL drops to the 40-ml VOA vial. The number of drops should be determined on the additional sample and then discard that sample. For analyses other than VOCs, the pH can be confirmed by removing an aliquot with a pipet and placing the aliquot on the pH paper. The pH paper must not be placed directly into the sample.

4.4.8 Wipe Sampling Procedures

Wipe samples will be collected in accordance with the procedures defined in SOP ADL-1023, which are summarized as follows:

- All equipment used to collect samples will be cleaned before use and between samples in accordance with SOP USA-1008;
- Place a decontaminated stainless steel template onto area of surface to be sampled. If the site is not easily marked with the template (i.e., an irregular non-planar surface), write a detailed description, with measurements from easily identifiable objects, of the area sampled;
- With tweezers or forceps, remove sampling gauze (pre-moistened with preservative or hexane, depending on the analyte) from the pre-labelled sample vial;
- Wipe the area from left to right in rows from the top to the bottom of the framed sampling area, using uniform pressure;
- Wipe the same area in columns from the top to the bottom from the left side to the right side of the framed sampling area, using uniform pressure;
- Replace the gauze in the pre-labelled sample vial; and
- Fill out the appropriate chain of custody forms and prepare the sample for storage and shipping.

4.4.9 Sample Location and Elevation Survey Procedures

All sampling points will be plotted on an installation map. Where sediment, soil, and surface water samples are involved, as well as geophysical survey grids, sampling point coordinates (Universal Transverse Mercator) will be established from a USGS Topographic Map. If required by a specific Delivery Order, the location and elevation of existing ground water monitoring wells and other sampling points will be determined by a licensed surveyor. All locations will be recorded in a dedicated field notebook, entered in the USAEC IRDMIS, and located on an installation map.

4.4.10 Investigation-Derived Waste Handling Procedures

Potentially hazardous wastes to be generated could include drill cuttings, drill fluids, decontamination fluids, and protective clothing. These materials will be segregated and analyzed using a 45-minute PID headspace analysis test for volatile organic compounds. A headspace test, however, is unlikely to be appropriate for analysis of protective clothing and certain other types of wastes. This type of material will be disposed on site at a location approved by the EMO.

All drill cuttings and hand auger spoils will be placed on 6 mil polyethylene sheeting upon generation. If the material passes the headspace test it will be disposed of at the site of collection. If the material has greater than 10 parts per million volatiles, the material will be containerized and tested for Resource Conservation and Recovery Act (RCRA) toxicity using the Toxicity Characteristic Leachate Procedure (TCLP). If the material passes the TCLP, the material will be disposed of at a Fort Devens location specified by the Environmental Management Office (EMO).

If the material is classified as a RCRA hazardous waste, it will be disposed of in accordance with 40 CFR Part 262, *Standards Applicable to Generators of Hazardous Waste* and the Fort Devens Environmental Office. Sampling and TCLP analysis of the drums will be completed under this subtask. It is assumed that Fort Devens will provide support in moving the drums from the point of generation to a common storage area to be designated. We have tentatively selected Clean Harbors, Inc. to provide the transport and disposal of the RCRA hazardous waste generated during this investigation.

4.4.11 Geoprobe® Sampling

Soil and ground water samples will be collected using a truck-mounted Geoprobe® System. Samples may be collected for submittal to a laboratory for chemical analysis or may be analyzed for total petroleum hydrocarbons using a portable non-dispersive infrared (NDIR) analyser.

The Geoprobe® Sampling System consists of 3.0' lengths of small diameter (1" O.D. to 1.6" O.D.) stainless steel casing which are driven by percussion hammer into the subsurface. This system can be fitted with either the large bore soil sampler or the screen

point ground water sampler, depending on the desired sample media. No drill cuttings are produced from the probe.

The large bore soil sampling system will be used to collect soil core samples. The sampler is driven to the sample depth completely sealed. At the top of the sample interval, a small stop pin is removed and the sampler is driven approximately 2-feet, and then retracted to collect a sample. The sample is removed and retained in a 1.125" x 22" sleeve constructed of non-reactive materials (i.e. teflon, stainless steel).. The sample is removed from the sleeve and placed in a decontaminated stainless steel bowl and composited prior to distribution into the appropriate sample containers. A clean dedicated sleeve is used for each sample.

The screen point ground water sampler will be used to collect ground water samples. The sampler is driven to the sample depth and a small diameter screen is retracted from the sample sheath. A polyethylene tube with a stainless steel check valve is then inserted through the sampler to the depth of the screen and a ground water sample is collected.

During soil sampling, the Geoprobe® casing/sampler, stainless steel spoon and stainless steel bowl and any sampling equipment which comes into contact with the sample media will be decontaminated before collecting each sample in accordance with SOP USA-1008. The acetate sleeves are dedicated to each sample and are disposed of after use.

During ground water sampling, the Geoprobe® and the stainless steel check valve will be decontaminated between sample points in accordance with SOP USA-1008. The polyethylene tubing used to extract ground water samples will be dedicated to each sample location and will not require decontamination.

4.4.12 Ambient Air Sampling

Ambient air samples will be collected and analyzed by subcontracted laboratories.

4.4.13 Sediment and Surface Water Bioassays (Toxicity Testing)

Sediment and surface water samples will be collected for sediment, sediment elutriate (pore water), and surface water bioassay tests in accordance with the methods described in Section 7.4.2.3. Samples will be collected following procedures outlined in the Quality Assurance Project Plan and in Standard Operating Procedures ADL-1024 and USA-1001, included in Volume II of the QAPjP. Due to the large sample volumes required for the bioassays, the samples will be composite samples and sample containers will consist of six-gallon stainless steel containers with lids. Samples will be collected in proximity to locations of sediment and surface water samples for chemical analysis to allow comparison of bioassay results with total contaminant levels.

5.0 Sample Custody

This section describes procedures for sample chain-of-custody to be followed by Arthur D. Little sampling personnel and the subcontracted laboratory. The primary objective of the chain-of-custody procedures is to provide an accurate written record that can be used to trace the possession and handling of a sample from the moment of its collection through its analyses. A sample is considered to be in custody if it is: in someone's physical possession; in someone's view; locked up; or kept in a secured area that can only be accessed by authorized personnel.

The purpose of these procedures is to ensure that the integrity of the samples is maintained during sample collection, transportation, storage, and analysis.

Sample identification documents must be carefully prepared so that sample identification and chain-of-custody can be maintained and sample disposition controlled. Sample identification documents include field notebooks, sample labels, custody seals, and chain-of-custody records. An example of the custody form is provided in Figure 5-1.

5.1 Field Custody Procedures

The field custody procedures to be followed by the field sampling crew are summarized in this section. The specific field custody SOPs to be used during this investigation are listed in Figure 4-1 to this QAPjP. All SOPs have been prepared in accordance with the programmatic QA requirements specified by USAEC and U.S. EPA. The Delivery Order Specific supplements provide the site identification and sample identification system to be applied to all samples collected during Fort Devens investigations.

As appropriate, specific site and sample identification codes for Fort Devens Delivery Orders are provided in Work Plans.

5.2 Laboratory Custody Procedures

The laboratory chain-of-custody of the samples begins with sample receipt and continues through final disposition of the field samples and other analytical samples (e.g., extracts) generated during analysis. The areas of concern for laboratory custody of samples include the following: sample receipt and log-in; internal chain-of-custody

Arthur D Little SAMPLE TRACKING SYSTEMS

USAEC

CHAIN OF CUSTODY RECORD

Case No. _____ COC By: _____

ADL Field Sampler Initials (3)	Time of Sampling (Military Clock) (4)	Site ID (10)	Field Sample Number (8)	File/ Media Type (3)	Site Type (4)	Depth Ft. (5)	Sample Techniques (1)	Sample Flag Code (1)	Sample QC Code (1)	TEST NAME / CODE																		Matrix	Number of Containers

Relinquished by: Arthur D. Little, Inc.

Date: _____ Time: _____ Signature: _____

Carrier: _____ Air Bill Number: _____ Total No. of Containers

Accepted by:

Date: _____ Time: _____ Signature: _____

Relinquished by:

Date: _____ Time: _____ Signature: _____

Accepted by:

Date: _____ Time: _____ Signature: _____

Comments:

Figure 5-1: Example of Chain-of-Custody Record

during analysis; sample lotting and labeling; sample splitting; storage of samples and sample extracts; and disposal.

A copy of applicable field chain-of-custody records will be maintained with each sample. In addition, each lot of samples will be maintained under separate laboratory chain-of-custody records which include: the unique laboratory sample identification number; date and time of collection, preparation and analysis; source of sample; analyses required; signatures of laboratory personnel relinquishing and receiving sample custody, and any other pertinent information.

For Fort Devens investigations, custody of field samples will be relinquished to the subcontracted laboratory at the time of sample receipt and log-in. Specific procedures will be followed by the laboratory to ensure maintenance of an accurate written record that can be used to trace the possession and handling of a sample from the moment of its collection through its analysis and disposal and to ensure that the integrity of the sample is maintained throughout the analytical process.

DataChem Laboratories has prepared SOPs for all aspects of sample custody during the analytical phase of the investigation; these SOPs conform to the requirements of the USATHAMA QA program. The laboratory custody procedures are summarized in the DataChem QA Program Plan for USAEC Laboratory Analysis provided in Appendix A of this QAPjP; the appropriate SOPs are listed in Figure 4-1.

6.0 Calibration Procedures and Frequency

This section presents information regarding the calibration of field and laboratory instrumentation to be used by Arthur D. Little and the subcontracted analytical laboratory during Fort Devens investigations. All instruments and equipment used during sampling and analysis will be operated, calibrated, and maintained according to the manufacturer's guidelines and recommendations, as well as the criteria set forth in the applicable field and laboratory procedures addressed in this section. Operation, calibration, and maintenance and calibration information will be maintained in an appropriate logbook or reference file for each instrument. If daily calibration cannot be achieved an alternate instrument which can achieve calibration will be used.

A description of the calibration procedures or reference to applicable SOPs is provided in the sections below. Calibration standards and frequency requirements are also summarized. Additional analytical method-specific calibration information is provided in the QA Program for the analytical laboratory (Appendix A) for USAEC-approved analyses and within the analytical methods for the non-USAEC analyses (Appendix C).

Two types of calibration are discussed in this section:

- Operational calibration, which is routinely performed as part of instrument usage, such as the development of a standard curve for use with an atomic absorption spectrophotometer. Operation calibration is generally performed for instrument systems.

- Periodic calibration, which is performed at prescribed intervals for equipment, such as balances and thermometers. In general, equipment which can be calibrated periodically is a distinct, singular purpose unit and is relatively stable in performance.

6.1 Field Instrumentation

All field instrumentation will be maintained according to manufacturer's recommendations, including those regarding initial and routine calibration, as outlined in the appropriate operating manual. Maintenance and calibration procedures will be documented in the instrument logbook. In general, instruments will be calibrated at

the start of each day of sampling and at the end of the day to check for instrument drift. All calibration data and calibration checks will be entered into the field notebook. Failure of an instrument to maintain accurate calibration will be reported to the site coordinator who will take immediate action to ensure that accurate field data are collected. The faulty instrument will be tagged and will not be used until it has been repaired or recalibrated.

Field measurements will be made for the following parameters: pH, temperature, conductivity, and turbidity. Total volatile organic emissions data will be collected in the field for Health and Safety purposes and for VOC contaminant screening purposes.

The instruments used to obtain field pH, temperature, conductivity, and turbidity measurements are factory calibrated and are routinely checked for accuracy against known standards; if necessary, recalibration will be performed. The specific procedures used to check the accuracy of these various field instruments are summarized below. SOPs for use and calibration of each of the field instruments are provided in Figure 4-1.

- pH: The accuracy of pH measurements obtained in the field is ensured by calibrating the pH meter against standard buffer solutions of known pH. The pH electrode is initially calibrated against a pH 7.0 buffer and then recalibrated at either pH 4.0 or 10.0 (depending on the anticipated range of sample pH). These procedures are performed at the beginning of each day of field sampling activities and at the end of the day to check for drift. The procedures for use and calibration of the pH meter are provided in SOP ADL-5013;

- Temperature: The accuracy of the field instrumentation used to obtain temperature data will be checked against a NBS thermometer at the beginning of each day of sampling and again at the end of the day to check for instrument drift;

- Conductivity: The accuracy of the conductivity meter will be checked daily during field sampling activities. A standard potassium chloride solution of known conductivity (0.1 N KCl) will be used; if necessary, recalibration of the instrument will be performed as indicated in SOP ADL-5011; and

- Turbidity: The accuracy of the turbidity meter will be checked against a standard of known turbidity (0.02 NTU) before each reading in the field. The procedures for use and calibration of the turbidity meter are provided in SOP ADL-5026.

Data for total volatile organic emissions will be obtained in the field using a photoionization detector (PID). The procedures for use and calibration of the PID are provided in SOP ADL-5012. Calibration is verified prior to use in the field and at the beginning of each day of field sampling activities; calibration is verified at the end of the day to check for drift. There is isobutylene in air at a concentration of 25 to 100 ppm; calibration will be performed at ambient temperature and pressure.

An Explosimeter will be used to determine percent oxygen for Health and Safety purposes and will be calibrated as follows:

- The instrument will be inspected and calibrated on a daily basis;
- The instrument will be inspected to ensure that entry and exit ports are clear;
- Turn the switch to the ON position. At this point the alarm will sound and the meter dials will jump;
- Allow the meters to stabilize and press the red RESET button. If the alarm continues, turn switch to HORN OFF position;
- Check the battery by depressing the black BATTERY button and note reading on the explosimeter display;
- Calibrate the oxygen meter to 20.8 percent by using the CALIBRATE knob;
- Zero the explosimeter to zero with the ZERO knob;
- If horn was turned off, return the switch to the ON position; and
- Check alarm levels by adjusting the CALIBRATE knob for oxygen levels and the ZERO know for explosimeter levels and note readings when alarm sounds. Return readings to normal and depress RESET button.

6.2 Laboratory Calibration

The laboratory analyses for samples collected during the investigations undertaken in this project will be performed by DataChem Laboratories. All analytical instruments and equipment used in DataChem Laboratories are controlled by a formal calibration program. The program verifies that equipment is of the proper type, range, accuracy, and precision to provide data compatible with the specified requirements of the

investigation. Calibration is performed internally by laboratory personnel using reference standards or externally by calibration agencies or equipment manufacturers.

This section prescribes the routine laboratory practices used to implement a calibration program. Development and documentation of the laboratory calibration program is the responsibility of the Laboratory Managers. Implementation is the responsibility of the supervisors and analysts; and the Laboratory Quality Assurance Coordinator (QAC) monitors the procedures.

6.2.1 Laboratory Instrumentation Calibration

6.2.1.1 Calibration Standards. Two types of reference standards are used for calibration of laboratory instrumentation:

- Physical standards, such as weights for calibrating balances and certified thermometers for calibrating working thermometers, refractors and ovens, which are generally used for periodic calibration; and

- Chemical standards, such as Standard Reference Materials (SRMs) provided by the National Institute of Standards and Technology (NIST) or the U.S. EPA. These may include vendor-certified materials traceable to NIST or U.S. EPA SRMs. These are primarily used for operational calibration.

Whenever possible, physical reference standards have known relationships to nationally recognized standards (e.g., NIST) or accepted values of natural physical constants. If national standards do not exist, the basis for the reference is documented.

Physical reference standards are used only for calibration and are stored separately from equipment used in analyses. In general, physical reference standards are at least four to ten times as accurate as the requirements for the equipment which they are used to calibrate. In general, physical standards are recalibrated annually by a certified external agency.

Whenever possible, chemical reference standards are directly traceable to NIST SRMs. If SRMs are not available, compounds of vendor-certified high purity are used to prepare calibration standards.

6.2.1.2 Calibration Frequency. Instruments and equipment shall be calibrated at prescribed intervals and/or as part of the operational use of the equipment. Frequency shall be based on the type of equipment, inherent stability, manufacturer's recommendations, values provided in recognized standards, intended data use,

specified analytical methods, effect of error upon the measurement process, and prior experience.

Equipment that cannot be calibrated or becomes inoperable during use is removed from service and tagged to indicate it is out of calibration. Such equipment must be repaired and satisfactorily recalibrated before reuse. For equipment that fails calibration, Nonconformance Record (NCR) is used to record the corrective action and to demonstrate satisfactory calibration.

The following data-generating laboratory instruments require *annual calibration.*

- Analytical Balance

The following data-generating laboratory instruments require *semi-annual calibration.*

- UV-VIS Spectrophotometer

The following data-generating laboratory instruments require *calibration before each use.*

a. The first group includes the instruments for which the calibration procedure is the establishment of a calibration curve.

   (1) UV-VIS Spectrophotometer (when used for relative analyses)
   (2) Technicon Autoanalyzer
   (3) Total Organic Carbon Analyzer
   (4) Atomic Absorption Spectrophotometer
   (5) IR Spectrophotometer
   (6) Selective Ion Meter
   (7) Inductively Coupled Plasma/Atomic Emission Spectrophotometer

b. The second group includes instruments for which the calibration procedure is the measurement of standard response factors as described in the individual analytical methods. The documentation of the calibration is the record of standard concentrations and responses stored in the files of the standard runs.

   (1) Gas Chromatograph
   (2) Gas Chromatograph/Mass Spectrometer

c. The third group includes instruments for which the calibration procedure consists of the measurement of one or two standards. From the standard measurements either the instrument is set to read the appropriate value or a calibration factor is calculated. The results of the standard measurements are recorded on the laboratory data sheets.

(1) pH Meter
(2) Selective Ion Meter (when used for pH measurements)
(3) Conductivity Meter
(4) Dissolved Oxygen Meter
(5) Turbidimeter/Nephelometer

6.2.1.3 Tuning and GC/MS Mass Calibration. Prior to initiating any ongoing data collection, it is necessary to establish that a given GC/MS meets the standard mass spectral abundance criteria. This is accomplished through the analysis of decafluorotriphenylphosphine (DFTPP) or p-bromofluorobenzene (BFB). The ion abundance criteria for each calibration compound *must* be met before any samples, blanks, or standards can be analyzed.

6.2.1.4 Decafluorotriphenylphosphine (DFTPP). Each GC/MS system used for the analysis of semivolatile or pesticide compounds must be hardware-tuned to meet the abundance criteria for a 50-ng injection of decafluorotriphenylphosphine (DFTPP). DFTPP may be analyzed separately or as part of the calibration standard. The criteria must be demonstrated daily or for each 12-hour period, whichever is more frequent. DFTPP must be injected to meet this criterion. Post-acquisition manipulation of ion abundance is *not* acceptable. Documentation of the calibration is provided in the form of a mass listing (Table 6-1).

6.2.1.5 p-Bromofluorobenzene (BFB). Each GC/MS system used for the analysis of volatile compounds must be hardware-tuned to meet the abundance criteria for a maximum of a 50-ng injection of BFB. Alternately, 50 ng of BFB solution is added to 5.0 mL of reagent or standard solution and analyze. This criterion must be demonstrated daily or for each 12-hour period, whichever is more frequent. Post-acquisition manipulation of ion abundance is *not* acceptable. Documentation of the calibration is provided in the form of a mass listing (Table 6-2).

DFTPP and BFB criteria *must* be met before any samples, sample extracts, blanks, or standards are analyzed. Any samples analyzed when tuning criteria have not been met may require reanalysis at no cost to the client.

Definition: The 12-hour period for tuning and calibration criteria begins at the moment of injection of the DFTPP and BFB analysis that the laboratory submits as documentation of complaint tune. The period ends after 12 hours according to the system clock.

6.2.2 Operational Calibration

Operational calibration is generally performed as part of the analytical procedure. Included may be the analysis of a method blank and the preparation of a standard response (standard calibration) curve. Following is a brief discussion of the analysis of method blanks and preparation of standard curves.

6.2.2.1 General Calibration Procedures. The initial phase of a laboratory testing program requires the selection and certification of the method best suited for an individual parameter. Certification, or verification, is the elimination, or minimizing, of determinate errors which may be due to analyst error or the use of less- than-optimum equipment, reagents, solvents, or gases. The quality of materials, even though they are analytical reagent (AR) grade or better, may vary from one source to another. The analyst must determine, through the use of reagent and/or solvent blanks, if materials are free from interfering substances which could affect the analysis. Other steps in certifying the method include the determination of a method blank and the preparation of a standard calibration curve.

6.2.2.2 Method Blank. The analyst will prepare a method blank to evaluate background levels of contamination associated with sample preparation and analysis. The method blank will be prepared and analyzed in the same manner as field samples using all reagents used in processing the samples. In the USAEC program, a method blank must be used at a frequency of one per lot and is prepared using the standard water or soil matrix. The standard water matrix consists of Type I water for inorganic analyses and Type II water containing 100 mg/l of chloride and sulfate for organic analyses. The standard soil matrix is provided to the laboratory by USAEC.

6.2.2.3 Calibration Curve. For all "relative" analyses, a calibration or standard curve is required to calculate sample concentrations from the measured instrument responses. A calibration curve is prepared by measuring the instrument responses for a series of standard solutions of the analyte. The sample concentrations are then calculated by comparison to the standard points. One means to perform these calculations is to use regression analysis to fit a curve through the standard data. The sample concentrations can then be calculated using the resulting regression equation. The regression analysis also provides parameters which can be used to assess the condition of the analysis. The majority of analyses in the laboratory give linear calibration curves or can be transformed to a linear form. Other analyses can be fitted to a parabolic curve.

6.2.3 Calibration for USAEC-Approved Methods

The *USATHAMA Quality Assurance Program* delineates, in detail, the requirements for instrument calibration, initial calibration for analysis, and daily calibration during sample analysis. DataChem Laboratories has implemented the USAEC specifications for all approved methods. The specific calibration procedures for USAEC-approved methods are summarized in the DataChem QA Program Plan provided in Appendix A.

Table 6-1 summarizes the general instrumental systems controls associated with the USAEC calibration program. The concentration range of the calibration standards brackets the certified range of the method. For the minimum testing range (MTR), initial calibration for Class I methods includes a minimum of one blank and five levels of calibration standards plus the check standard; for Class 1A methods, initial calibration includes a minimum of one blank and three levels of calibration standards. When order-of-magnitude extensions are performed, additional high level standards are required.

Initial calibration procedures are performed in the following events:

- The first day that USAEC-approved methods are performed;
- The instrument is started up (other than daily start-up and shut-down);
- The instrument is used to analyze analytes different from those for which the instrument was previously calibrated; and
- The instrument fails daily calibration.

Daily calibration procedures are performed each day of instrumental analysis to verify that the instrument response has not changed from the previous calibration.

Calibration and spiking standards are prepared from Standard Analytical Reference Materials (SARMS) or interim SARMS obtained from the USAEC Repository Program, whenever possible. Materials purchased from outside vendors are classified as "off-the-shelf" and used only when SARMS are not available. Off-the-shelf materials are characterized against NIST or U.S. EPA standards for purity and identification. Standards characterization data are kept on file at the laboratory. Chain-of-custody procedures are maintained for all standard reference materials. Materials are stored in locked areas at ambient temperature or below 4°C for inorganics and organics, respectively.

Table 6-1: DFTPP Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria
51	30.0 - 60.0 percent of mass 198
68	less than 2.0 percent of mass 69
70	less than 2.0 percent of mass 69
127	40.0 - 60.0 percent of mass 198
197	less than 1.0 percent of mass 198
198	base peak, 100 percent relative abundance
199	5.0 - 9.0 percent of mass 198
275	10.0 - 30.0 percent of mass 198
365	greater than 1.0 percent of mass 198
441	present but less than mass 443
442	greater than 40.0 percent of mass 198
443	17.0 - 23.0 percent of mass 442

Note: Whenever the Laboratory takes corrective action which may change or affect the tuning criteria for DFTPP (e.g., ion source cleaning or repair, etc.), the tune is verified irrespective of the 12-hour tuning requirements.

Table 6-2: BFB Key Ions and Abundance Criteria

Mass	Ion Abundance Criteria
50	15.0 - 40.0 percent of the base peak
75	30.0 - 60.0 percent of the base peak
95	base peak, 100 percent relative abundance
96	5.0 - 9.0 percent of the base peak
173	less than 2.0 percent of mass 174
174	greater than 50.0 percent of the base peak
175	5.0 - 9.0 percent of mass 174
176	greater than 95.0 percent but less than 101.0 percent of mass 174
177	5.0 - 9.0 percent of mass 176

Note: Whenever the Laboratory takes corrective action which may change or affect the tuning criteria for BFB (e.g., ion source cleaning or repair, etc.), the tune must be verified irrespective of the 12-hour tuning requirements.

7.0 Analytical Procedures

7.1 Analytical Program

The chemical analysis program for Fort Devens investigations is directed towards generating data from field and laboratory tests that will define contamination characteristics at the Fort Devens site and support the determination of the need for further action. Specific sets of analytes for laboratory analysis are specified for each sample collected from the site. The chemical analysis program has been designed to obtain quantitative data on the presence of these selected chemicals at detection limits consistent with USAEC target reporting limits and federal and state regulations. In addition to measuring the concentration of specific analytes, all tentatively identified organic compounds (TIC) detected [when GC/MS analyses (VOCs and SVOCs) are conducted], with an area of greater than 10% of the internal standard must be library searched. This technique lends some assurance that major organic species that may be present in the Fort Devens samples will be detected and reported. As an indicator of a broader spectrum of oil-related contamination, total petroleum hydrocarbons (TPHC) may be measured at selected locations. This technique indicates the presence of contamination from a variety of oils and/or fuels that may have been used at Fort Devens. Tests for total volatile organic emissions will also be conducted in the field to provide "real time" information about ground water well development and the presence of broad indicators of contamination, in soil, water, and air (headspaces and/or soil gases).

Table 7-1 presents a listing of the analyses that could be performed on the samples collected during the Fort Devens investigations. Table 7-2 provides a complete list of analytes. For each of the analyses, the reference analytical method is provided. The analyses to be conducted for each Delivery Order are specified in the supplements; any exceptions to the lists provided in Table 7-2 are also in the supplements. Most of the analyses cited in Table 7-1 will be performed using USAEC-approved methods. The referenced USAEC-approved methods are unique to DataChem Laboratories and all USAEC-approved analyses are conducted according to the requirements of the specific method, without deviation. For the TCLP organics and inorganics, an EPA-approved method is used. The TCLP analyses are performed on investigation-derived waste samples and are not part of the site characterization data base. The TPHC method is a non-USAEC method based on EPA and ASTM methods.

Table 7-1: Summary of Analytical Methods for Site Characterization

Analysis-Matrix	Method Type	USAEC-Approved Method Number*	Comparable EPA Method Number**
TCL Volatiles - soil/sediment	Class 1A	LM23	SW-846; 8240
TCL Volatiles - water	Class 1A	UM21	SW-846; 8240
TCL Semivolatiles - Water	Class 1A	UM25	SW-846; 8270
TCL Semivolatiles - soil/sediment	Class 1A	LM25	SW-846; 8270
TCL PEST/PCBs - soil/ sediment	Class 1	LH17	SW-846; 8080
TCL Pesticides/PCBs - water	Class 1	LH17	SW-846; 8080
Explosives - soil/sediment	Class 1	LW23	NA
Explosives - water	Class 1	UW25	NA
TAL Metals (ICP) - water	Class 1	SS12	SW-846; 6010
TAL Metals (ICP) -soil/sediment	Class 1	JS12	SW-846; 6010
Mercury - water	Class 1	CC8	SW-846; 7471
Mercury - soil/sediment	Class 1	Y9	SW-846; 7471
Chloride/Sulfate - water	Class 1	TT09	EPA 300.0
Chloride/Sulfate - soil/sediment	Class 1	KT07	EPA 300.0
Nitrate - water	Class 1	LL8	EPA 353.2
Nitrate - soil/sediment	Class 1	KF17	EPA 353.2
Organophosphorus Pesticides - soil/sediment	Class 1	LH15	SW-846; 8140
Organophosphorus Pesticides - water	Class 1	UH11	SW-846; 8140
Herbicides - soil/sediment	Class 1	LH18	SW-846; 8150
Herbicides - water	Class 1	UH10	SW-846; 8150
Phosphate - soil/sediment	Class 1	KF18	EPA 365.1
Phosphate - water	Class 1	TF29	EPA 365.1

Table 7-1: Summary of Analytical Methods for Site Characterization (continued)

Analysis-Matrix	Method Type	USAEC-Approved Method Number*	Comparable EPA Method Number**
Phosphorus - water	Colorimetric	Non-USAEC	EPA 365.1
Total Petroleum Hydrocarbons (TPHC) - soil/sediment	Infrared***	Non-USAEC	EPA 418.1
Total Petroleum Hydrocarbons (TPHC) - water	Infrared***	Non-USAEC	EPA 418.1
Total Organic Carbon - soil/sediment	Combustion***	Non-USAEC	EPA 415.1
Asbestos - soil/sediment	Polarized Light Microscopy	Non-USAEC	NIOSH 9002
Total Kjeldahl Nitrogen (TKN) - water	Class 1	TF28	EPA 351.2
Hardness - water	Colorimetric***	Non-USAEC	EPA 130.1
Alkalinity - water	Colorimetric***	Non-USAEC	EPA 310.1
Total Suspended Solids (TSS) - water	Gravimetric***	Non-USAEC	EPA 160.2

* USAEC-approved method numbers are unique to DataChem Laboratories. Analyte CRLs for USAEC-approved methods are on file at Arthur D. Little.

** References: Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, March 1983. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, January 1990.

*** Non-USAEC analytical methods are provided in Appendix C.

NA Not Applicable. There is no comparable EPA method for this USAEC method.

Table 7-2: Summary of Specific Constituents in Multi-Analyte Methods

TCL Volatile Organic Compounds	ANALYTE CODE
1,1,1-TRICHLOROETHANE	111TCE
1,1,2-TRICHLOROETHANE	112TCE
1,1-DICHLOROETHENE	11DCE
1,1-DICHLOROETHANE	11DCLE
1,2-DICHLOROETHENES (CIS AND TRANS)	12DCE
1,2-DICHLOROETHANE	12DCLE
1,2-DICHLOROPROPANE	12DCLP
1,3-DICHLOROPROPENE	13DCPE
2-CHLOROETHYLVINYL ETHER	2CLEVE
ACETONE	ACET
BROMODICHLOROMETHANE	BRDCLM
CIS-1,3-DICHLOROPROPENE	C13DCP
VINYL ACETATE	C2AVE
VINYL CHLORIDE	C2H3CL
CHLOROETHANE	C2H5CL
BENZENE	C6H6
CARBON TETRACHLORIDE	CCL4
METHYLENE CHLORIDE	CH2CL2
BROMOMETHANE	CH3BR
CHLOROMETHANE	CH3CL
BROMOFORM	CHBR3
CHLOROFORM	CHCL3
CHLOROBENZENE	CLC6H5
CARBON DISULFIDE	CS2
DIBROMOCHLOROMETHANE	DBRCLM
ETHYLBENZENE	ETC6H5
TOLUENE	MEC6H5
METHYL ETHYL KETONE	MEK
METHYL ISOBUTYL KETONE	MIBK
STYRENE	STYR
TRANS-1,2-DICHLOROETHENE	T12DCE
TRANS-1,3-DICHLOROPROPENE	T13DCP
1,1,2,2-TETRACHLOROETHANE	TCLEA
TETRACHLOROETHENE	TCLEE
TRICHLOROETHENE	TRCLE
XYLENES, TOTAL	TXYLEN
	TCFM
	DCFM

TAL Metals	
SILVER	AG
ALUMINUM	AL
ARSENIC	AS
BARIUM	BA
BERYLLIUM	BE
CALCIUM	CA
CADMIUM	CD
COBALT	CO
CHROMIUM	CR
COPPER	CU
IRON	FE
MERCURY	HG
POTASSIUM	K
MAGNESIUM	MG
MANGANESE	MN
SODIUM	NA
NICKEL	NI
LEAD	PB
ANTIMONY	SB
SELENIUM	SE
THALLIUM	TL
VANADIUM	V
ZINC	ZN

Table 7-2: Summary of Specific Constituents in Multi-Analyte Methods

TCL Semivolatile Organic Compounds	ANALYTE CODE
1,2,4-TRICHLOROBENZENE	124TCB
1,2-DICHLOROBENZENE	12DCLB
1,3-DICHLOROBENZENE	13DCLB
1,4-DICHLOROBENZENE	14DCLB
2,4,5-TRICHLOROPHENOL	245TCP
2,4,6-TRICHLOROPHENOL	246TCP
2,4-DICHLOROPHENOL	24DCLP
2,4-DIMETHYLPHENOL	24DMPN
2,4-DINITROPHENOL	24DNP
2,4-DINITROTOLUENE	24DNT
2,6-DINITROTOLUENE	26DNT
2-CHLOROPHENOL	2CLP
2-CHLORONAPHTHALENE	2CNAP
2-METHYLNAPHTHALENE	2MNAP
2-METHYLPHENOL / 2-CRESOL	2MP
2-NITROANILINE	2NANIL
2-NITROPHENOL	2NP
3,3'-DICHLOROBENZIDINE	33DCBD
3,4-DINITROTOLUENE	34DNT
3-NITROANILINE	3NANIL
3-NITROTOLUENE	3NT
4,6-DINITRO-2-CRESOL / METHYL-4,6-DINITROPHENOL	46DN2C
4-BROMOPHENYLPHENYL ETHER	4BRPPE
4-CHLOROANILINE	4CANIL
4-CHLORO-3-CRESOL / 3-METHYL-4-CHLOROPHENOL	4CL3C
4-CHLOROPHENYLPHENYL ETHER	4CLPPE
4-METHYLPHENOL / 4-CRESOL	4MP
4-NITROANILINE	4NANIL
4-NITROPHENOL	4NP
ACENAPHTHENE	ANAPNE
ACENAPHTHYLENE	ANAPYL
ANTHRACENE	ANTRC
BIS (2-CHLOROETHOXY) METHANE	B2CEXM
BIS (2-CHLOROISOPROPYL) ETHER	B2CIPE
BIS (2-CHLOROETHYL) ETHER	B2CLEE
BIS (2-ETHYLHEXYL) PHTHALATE	B2EHP
BENZO [A] ANTHRACENE	BAANTR
BENZO [A] PYRENE	BAPYR
BENZO [B] FLUORANTHENE	BBFANT
BUTYLBENZYL PHTHALATE	BBZP
BENZOIC ACID	BENZOA
BENZO [G,H,I] PERYLENE	BGHIPY
BENZO [K] FLUORANTHENE	BKFANT
BENZYL ALCOHOL	BZALC
CHRYSENE	CHRY
HEXACHLOROBENZENE	CL6BZ
HEXACHLOROCYCLOPENTADIENE	CL6CP
HEXACHLOROETHANE	CL6ET
DIBENZ [A,H] ANTHRACENE	DBAHA
DIBENZOFURAN	DBZFUR
DIETHYL PHTHALATE	DEP
DIMETHYL PHTHALATE	DMP
DI-N-BUTYL PHTHALATE	DNBP
DI-N-OCTYL PHTHALATE	DNOP
FLUORANTHENE	FANT
FLUORENE	FLRENE
HEXACHLOROBUTADIENE	HCBD
INDENO [1,2,3-C,D] PYRENE	ICDPYR
ISOPROPYLAMINE	IPA
ISOPHORONE	ISOPHR
NAPHTHALENE	NAP
NITROBENZENE	NB
NITROSO DI-N-PROPYLAMINE	NDNPA
N-NITROSO DI-N-PROPYLAMINE	NNDNPA
N-NITROSO DIPHENYLAMINE	NNDPA
PENTACHLOROPHENOL	PCP
PHENANTHRENE	PHANTR
PHENOL	PHENOL
PYRENE	PYR

Table 7-2: Summary of Specific Constituents In Multi-Analyte Methods

Explosives	ANALYTE CODE
1,3,5-TRINITROBENZENE	135TNB
1,3-DINITROBENZENE	13DNB
2,4,6-TRINITROTOLUENE	246TNT
2,4-DINITROTOLUENE	24DNT
2,6-DINITROTOLUENE	26DNT
3,4-DINITROTOLUENE	34DNT
CYCLOTETRAMETHYLENETETRANITRAMINE	HMX
NITROBENZENE	NB
NITROCELLULOSE	NC
NITROGLYCERINE	NG
PENTAERYTHRITOL TETRANITRATE	PETN
CYCLOTRIMETHYLENETRINATRAMINE / CYCLONITE	RDX
N-METHYL-N,2,4,6-TATRANITROANILINE / NITRAMINE	TETRYL
TCL Pesticides/PCBs	
ALPHA-BENZENE HEXACHLORIDE	ABHC
ALPHA CHLORDANE	ACLDAN
ALPHA-ENDOSULFAN	AENSLF
ALDRIN	ALDRN
BETA-BENZENE HEXACHLORIDE	BBHC
BETA-ENDOSULFAN	BENSLF
DELTA-BENZENE HEXACHLORIDE	DBHC
DIELDRIN	DLDRN
ENDRIN	ENDRN
ENDRIN ALDEHYDE	ENDRNA
ENDRIN KETONE	ENDRNK
ENDOSULFAN SULFATE	ESFSO4
GAMMA-CHLORDANE	GCLDAN
HEPTACHLOR	HPCL
HEPTACHLOR EPOXIDE	HPCLE
LINDANE	LIN
METHOXYCHLOR	MEXCLR
PCB 1016	PCB016
PCB 1221	PCB221
PCB 1232	PCB232
PCB 1242	PCB242
PCB 1248	PCB248
PCB 1254	PCB254
PCB 1260	PCB260
2,2-BIS (PARA-CHLOROPHENYL) - 1,1-DICHLOROETHANE	PPDDD
2,2-BIS (PARA-CHLOROPHENYL) - 1,1-DICHLOROETHENE	PPDDE
2,2-BIS (PARA-CHLOROPHENYL) - 1,1,1-TRICHLOROETHANE	PPDDT
TOXAPHENE	TXPHEN
Organophosphorus Pesticides*	
ATRAZINE	ATRAZ
PARATHION	PARAT
METHYL PARATHION	MPARAT
MALATHION	MALATH
SUPONA	SUPO
VAPONA	VAPO
Water Quality Parameters	
CHLORIDE	CL
TOTAL NITROGEN	NIT
NO3-N	N03
SULFATE	S04
TOTAL PHOSPHOROUS	P4
HARDNESS	HARD
ALKALINITY	ALK
TOTAL SUSPENDED SOLIDS	TSS
DISSOLVED OXYGEN	DO

*The subcontracted laboratory is USAEC certified for the analysis of Atrazine, Parathion, Malathion, Supona, and Vapona. If it's deemed necessary by the USAEC Project Manager, the remainder of the organophosphorus organophosphorus Pesticides will be analyzed using the appropriate methods.

Table 7-2: Summary of Specific Constituents in Multi-Analyte Methods

Herbicides**	ANALYTE CODE
2,4,5-TRICHLOROPENOXYACETIC ACID	245T
2-(2,4,5-TRICHLOROPHENOXY) PROPIONIC ACID	245TP
2,4-DICHLOROPHENOXYACETIC ACID	24D
2,4-DB / 4-(2,4-DICHLOROPHENOXY) BUTYRIC ACID	24DB
TCLP Metals	
ARSENIC	AS
SILVER	AG
BARIUM	BA
CADMIUM	CD
CHROMIUM	CR
MERCURY	HG
LEAD	PB
SELENIUM	SE
TCLP Volatiles	
1,1-DICHLOROETHYLENE / 1,1-DICHLOROETHENE	11DCE
1,2-DICHLOROETHANE	12DCLE
BENZENE	C6H6
CARBON TETRACHLORIDE	CCL4
CHLOROFORM	CHCL3
CHLOROBENZENE	CLC6H5
METHYLETHYL KETONE / 2-BUTANONE	MEK
TETRACHLOROETHYLENE / TETRACHLOROETHENE	TCLEE
TRICHLOROETHYLENE / TRICHLOROETHENE	TRCLE
TCLP BNAs	
1,4-DICHLOROBENZENE	14DCLB
2,4,5-TRICHLOROPHENOL	245TCP
2,4,6-TRICHLOROPHENOL	246TCP
2,4-DINITROTOLUENE	24DNT
2-METHYLPHENOL / 2-CRESOL	2MP
3-METHYLPHENOL / 3-CRESOL	3MP
4-METHYLPHENOL / 4-CRESOL	4MP
CHLOROETHENE / VINYL CHLORIDE	C2H3CL
HEXACHLOROBENZENE	CL6BZ
HEXACHLOROETHANE	CL6ET
HEXACHLOROBUTADIENE	HCBD
NITROBENZENE	NB
PENTACHLOROPHENOL	PCP
PYRIDINE	PYRDIN
TCLP Pesticides	
CHLORDANE	CLDAN
ENDRIN	ENDRN
HEPTACHLOR	HPCL
LINDANE / GAMA-BENZENEHEXACHLORIDE / GAMA-HEXACHLOROCYCLOHEXANE	LIN
METHOXYCHLOR	MEXCLR
TOXAPHENE	TXPHEN
TCLP Herbicides	
2,4-DICHLOROPHENOXYACETIC ACID	24D
SILVEX	SILVEX

**The subcontracted laboratory is USAEC certified for the analysis of 2,4-D; 2,4,5-T, and 2,4,5-TD (Silvex). If it's deemed necessary by the USAEC Project Manager, the remainder of the Herbicides will be analyzed using the appropriate methods.

Details of the USAEC analyses, including the CRL for each analyte, are provided within the DataChem QA Program Plan provided in Appendix A to this QAPjP. A copy of the complete USAEC-approved DataChem method for each of these analyses will be maintained in the Arthur D. Little files for this project. The method and analyte approved procedures for the USAEC-approved methods are summarized in Sections 7.2 and 7.3, respectively. Brief summaries of the analytical methods to be used to generate site characterization data are provided in Section 7.4.

7.2 Laboratory Method Approval

In order to provide a common point of reference for all projects and to provide a means of evaluating laboratory performance, USAEC prescribes the use of standardized methods for commonly encountered analytes. These methods are sufficiently general to be used in almost any laboratory, yet specify all critical elements. The standardized methods are based on published methods of analysis, USAEC standing methods or past USAEC experience (e.g. for military unique compounds). Methods have been evaluated in terms of sound analytical practice and applicability to environmental projects. In addition to specifying sample preparation and analysis, each method also specifies calibration procedures and frequency, calibration check acceptance criteria, methods of preparing standard solutions, and preparation of QC samples.

Four different types of analyses are recognized by the *USATHAMA Quality Assurance Program*: Class 1, 1A, 1B, and Class 2; for specific Delivery Orders the class is specified in the supplements. The difference between the classes is the procedure used to characterize laboratory performance of the method. Class 1A certification is reserved exclusively for GC/MS methods; whereas Classes 1 and 1B are reserved for low sample-throughput methods (i.e., non-GC/MS). Class 2 certification is used for methods that screen for the presence or absence of contaminants. Each type of analysis requires a different level of documentation, including precision and accuracy data, and a different set of daily or batch-related QC criteria.

7.2.1 Laboratory Methods Requiring USAEC Approval

The Class 1 USAEC approved methods being used for the Fort Devens project are:

- Metals
- Nitrate
- Chlorinated Pesticides/PCBs
- Organophosphorus Pesticides
- Phosphorous
- Explosives
- Sulfate
- Chloride
- Herbicides
- Total Kjeldahl Nitrogen (TKN)

The Class 1A (GC/MS) USAEC approved methods being used for the Fort Devens project are:

- Volatile organics
- Semivolatile (acid/base/neutral) organics

7.2.2 Methods Not Requiring USAEC Approval

Some methods, including calibration of test and measurement equipment, do not require USAEC approval, due to either the nature of the measurement or the intended use of the data. When such methods are part of a project, USAEC will not provide a standardized method. However, laboratories must submit sufficient information in test plans, work plans, QAPjP, etc., to describe the procedures to be used. A copy of the methods must be submitted to the USAEC Chemistry Branch before it is used on any project.

The non-USAEC methods to be used for analysis of site characterization samples are for TSS (Total Suspended Solids), TPHC (Total Petroleum Hydrocarbons), TOC (Total Organic Carbon), Hardness, Alkalinity, Phosphate, and Asbestos (PLM). Copies of the proposed analytical methods for these analyses are provided in Appendix C of this QAPjP. Methods for analysis of hazardous waste characteristics, i.e., TCLP organics and inorganics, would also be non-certified methods. However, these analyses are not part of site characterization and apply only to disposal of investigation-derived waste.

7.3 Analyst Qualification

It is the responsibility of the organization to establish personnel qualifications and training requirements for all positions. Each member of the Fort Devens analytical team will have the education, training, technical knowledge, and experience, or a combination thereof, to enable that individual to perform their assigned functions. Personnel qualifications are documented in terms of education, experience, and training. Training is provided for each staff member to properly perform their functions.

Copies of the approved methods will be maintained by the laboratory QA staff and the Arthur D. Little Lead Chemist. Analysts will demonstrate their proficiency in conducting a particular chemical analysis by showing evidence of acceptable performance on past routine QC samples analyzed with each batch of samples. New analysts performing an established analytical procedure will be considered conditionally qualified until the first set of QA/QC data is generated. These QC data are required for every lot of samples analyzed. If these QC data are in control based on control charts, the analyst or analytical team will be considered qualified to run

that particular analysis. QC data that do not meet established QC requirements will be rejected, and corrective action, which may include re-analysis of the lot of samples and further training of the analytical team, will be taken.

The analysts and other subcontracted lab support personnel are responsible for adherence to the QA Program Plan and to the requirements of the USAEC program.

7.4 Analytical Methods

This section provides a brief summary of the USAEC-approved analytical methods, as well as non-USAEC methods, for the analysis of samples for this project.

7.4.1 Sulfate and Chloride

For these analyses, a small volume of sample, typically two to three milliliters, is introduced into an ion chromatograph (IC). The anions of interest are separated and measured using a system comprised of a guard column, separator column, suppressed column, and conductivity detector.

7.4.2 Volatile Organics (GC/MS)

The method for volatile organics is based on USEPA Method 8240 and is used to determine volatile organic compounds in a variety of matrices. An inert gas is bubbled through a 5-milliliter water sample or 5-gram soil sample contained in a specially designed purging chamber at ambient temperature. The purgeable organics are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent trap where the purgeables are trapped.

After purging is completed, the trap is heated and backflushed with the inert gas to desorb the purgeables onto a gas chromatographic column. The gas chromatograph (GC) is temperature programmed to separate the purgeables which are then detected with a mass spectrometer.

7.4.3 Semivolatile (Acid/Base/Neutral) Organics (GC/MS)

The method for semivolatiles is based on USEPA Method 8270 to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils, and ground water. For the analysis, a measured volume of sample, approximately 1 liter for aqueous samples or 30 grams for soil/sediment samples, is serially extracted with methylene chloride. The methylene chloride extract is dried, concentrated to a volume of one milliliter, and analyzed by GC/MS.

7.4.4 Organochlorine Pesticides/PCBs (GC/ECD)

The method for Organochlorine Pesticides/PCBs is based on USEPA Method 8080. For the analysis, a measured volume of sample, approximately one liter for aqueous samples and 10 grams for soil/sediment samples, is extracted with methylene chloride. The methylene chloride extract is dried and exchanged to hexane during concentration to a volume of 10 milliliters for less. The extract is separated by GC and the parameters are then measured with an electron capture detector. The method provides a Florisil column cleanup procedure and an elemental sulfur removal procedure to aid in the elimination of interferences that may be encountered.

7.4.5 Metals

7.4.5.1 Inductively Coupled Plasma Atomic Emission Spectroscopy (ICAP). For analysis, samples are solubilized or digested using a method based on USEPA Method 3010 for water and Method 3050 for soils. These methods are from "Test Methods for Evaluating Solid Waste," SW-846, third edition, USEPA, September 1986. The analysis procedure follows USEPA Method 6010 for multi-elemental determination of elements by ICAP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer and the intensities of the lines are monitored by photomultiplier tubes.

7.4.5.2 Cold Vapor (Mercury). The method for mercury analysis is based on USEPA Methods 7470 and 7471. Mercury-containing compounds from solid or aqueous samples are digested under acid conditions in the presence of heat and strong oxidant. Following digestion, mercury is reduced to its elemental state and aerated from solution in a cold vapor adsorption cell of fixed path length. The absorption cell is positioned in the light path of an atomic absorption spectrophotometer. Absorbance is measured (peak height) as a function of concentration at 253.7 nm. A calibration curve is constructed by plotting peak height concentration of known standards using a second order regression. The instrumental concentration is determined and the final sample concentration is calculated, accounting for any dilution or concentration process utilized and the initial volume of sample used for the analysis.

7.4.5.3 Graphite Furnace Atomic Absorption. USEPA reference methods for these analyses are Methods 7060 (arsenic), 7740 (selenium), 7421 (lead), 7841 (thallium), 3020 (water digestion), and 3050 (soil digestion).

Metallic constituents from solid or aqueous samples are made soluble through sample reflux digestion under acid conditions. Sample digestates are introduced into a temperature-programmed graphite furnace atomic absorption spectrophotometer (GFAA) which has been calibrated in accordance with specification. The sample is

dried, charred, and atomized. The metal atoms are placed in a beam of radiation by increasing the temperature, causing the specimen to volatilize. Characteristic radiation from a hollow cathode lamp is absorbed and the attenuated transmitted radiation is measured. Quantification of the analyte of interest in the digestate is based on a standard curve of absorption response versus known concentration using linear regression. The instrumental concentration is determined and the final sample concentration is calculated, accounting for any dilution or concentration process utilized.

7.4.6 Explosives

This method is based on USAEC Method CERTNF/UW25 (June 30, 1988) for aqueous samples and CERTNF/LW23 (June 14, 1988) for soils by HPLC.

For aqueous samples, the method employs solid phase extraction of 500 milliliters of an environmental water using a tube packed with Porapak R. The target analytes are desorbed with three milliliters of acetonitrile and the extract is diluted to a final volume of 10 milliliters with water. The analytes are separated by HPLC using isocratic elution and detected using ultraviolet absorbance (uv) at 250 nm.

For soil samples, the method employs extraction of one gram of an environmental soil using two milliliters of acetonitrile. Extraction is accomplished by vortexing followed by sonication of the sample for 18 hours. The resulting extract is filtered and diluted 1:8 with water. The target analytes are separated on a HPLC column using isocratic elution and detected using UV at 230 nm.

7.4.7 TSS (Total Suspended Solids)

The method that will be used for this analysis is USEPA Method 160.2. Suspended solids also known as non-filtrable residue is material that is retained by a standard glass fiber filter disk and remains after evaporation and drying to constant weight at 180°C. An aliquot of a 100 ml, or more, of well mixed sample is filtered through a glass fiber filter done under vacuum. The sample is then evaporated, dried in an oven for at least an hour at 180°, and weighted. The result is calculated by subtracting the weight of the filter from the weight of dried residue plus filter then dividing it by the volume of filtrate used.

7.4.8 TPHC (Total Petroleum Hydrocarbons by Infrared)

This method is based on USEPA Method 418.1. An aliquot portion of sample is extracted; 10mm infrared quartz cells are used for each analysis. Percent transmittance is measured and the concentration is determined by comparing the calculated absorbance against a calibration plot.

7.4.9 TOC in Sediment by IR

This method is based on USEPA Method 415.1. Organic carbon in a sample is converted to carbon dioxide by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector. The amount of CO_2 is directly proportional to the concentration of carbonaceous materials in the sample.

7.4.10 Total Phosphorous and Phosphate

These analyses are based on USEPA Method 365.1. For total phosphorous, an aliquot (20 mL) of the aqueous sample is combined with 5.0 mL of digestion reagent containing sulfuric acid, potassium sulfate and mercuric oxide, mixed with a vortex type mixer and digested for 2.5 hours between 200° and 380°C in a Technicon BD-40 block digester to convert all phosphorus to ortho-phosphate. The digestage is cooled, mixed with 20-ML ASTM Type I water and analyzed by automated flow injection analysis/spectrophotometry (Technicon AutoAnalyzer II with multi-test cartridge) in which a blue color is formed by the reaction with ascorbic acid at an acidic pH. The phosphomolybdenum complex is read at 660 nm. Phosphate in water or soil extract is determined by the direct colorimetric procedure without pretreatment of the sample.

7.4.11 Total Kjeldahl Nitrogen (TKN) in Water by Automated Spectrophotometry

This method is based on USEPA Method 351.2. An aliquot (20 mL) of the aqueous sample is combined with 5.0 mL of digestion reagent containing sulfuric acid, potassium sulfate and mercuric oxide, mixed with a vortex type mixer and digested for 2.5 hours between 200°C and 380°C in a Technicon BD-40 block digester to convert organic nitrogen to ammonium sulfate. The digestate is cooled, mixed with 20 mL of ASTM Type I water and analyzed by automated flow injection analysis/spectrophotometry (Technicon AutoAnalyzer II with multi-test cartridge).

The determination of nitrogen is based on a colorimetric method in which an emerald-green color is formed by the reaction of ammonia, sodium salicylate, sodium nitroprusside, and sodium hypochlorite (chlorine source) in a buffered alkaline medium at a pH of 12.8-13.0. The ammonia salicylate complex is read at 660 nm.

7.4.12 Organophosphorus Pesticides

The method for organophosphorus pesticides is based on USEPA Method 8140. This method provides gas chromatographic conditions for the detection of PPB levels of organophosphorus pesticides. Prior to analysis, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-µL aliquot of the extract is injected into a gas chromatograph, and compounds in the GC effluent are detected with a flame photometric or a nitrogen/phosphorus detector, operated in phosphorus-sensitive mode.

7.4.13 Chlorinated Herbicides

The method for chlorinated herbicides is based on USEPA Method 8150. This method provides extraction, esterification, and gas chromatographic conditions for the analysis of chlorinated acid herbicides. The esters are hydrolized with potassium hydroxide, and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography employing an electrolytic conductivity detector (ECD). The results are reported as the acid equivalents.

7.4.14 Nitrate

The method for nitrate, which is consistent with EPA Method 353.2, is based on the reaction of nitrate with brucine sulfate in 13 N sulfuric acid solution at 100°C. The sample is then placed on an automated spectrophotometer and measured for nitrate.

7.4.15 Hardness

Samples are digested with nitric acid and then 50 mLs of the sample is neutralized with ammonium hydroxide and analyzed by a colorimeter.

7.4.16 Alkalinity

Methyl orange is used as an indicator. Methyl orange is dissolved in a weak buffer at a pH of 3.1 which is used as the standard. Methyl orange is added to the samples and they are analyzed with an automated colorimeter. Any loss of color is directly proportional to the amount of alkalinity.

7.4.17 Asbestos (Bulk) by Polarizing Light Microscopy

The method to be used will be NIOSH 9002, which consist of a polarized light microscope with dispersion staining for asbestos identification.

7.4.18 Particle Size by Sieve Analysis

For this determination, Method ASTM D43-2 will be used. This method consists of size distribution analysis, for samples ranging in size from +1 to -400 mesh, using 8-inch diameter U.S. standard series sieves.

7.4.19 TCLP Leachate Preparation

For liquid wastes containing less than or equal to 0.5 percent dry solids, the waste is filtered through a 0.6 to 0.8 µm glass fiber filter. This is described as the TCLP extraction.

7.4.20 Volatile Organic Compounds (VOCs) in Ambient Air

The presence of VOCs in ambient air will be determined using EPA Method TO-14. This method utilizes a SUMMA® passivated stainless steel canister sampler with subsequent compound separation by gas chromatography and measurement by mass-selective detector or multi-detector techniques.The sampling technique uses an

evacuated 6-liter canister in which metered ambient air is pumped or drawn into the canister by the vacuum (referred to as pressurized or subatmospheric pressure sampling). Specific VOCs are stable for extended periods (up to 30 days), and can be measured at the parts per billion by volume (ppbv) level. Analysis involves using a high-resolution gas chromatograph (GC) coupled with one or more suitable non-specific GC detectors (i.e., NPD, FID, ECD, PID) or specific detectors (i.e., mass spectrometry with selected ion monitoring mode or scan mode, or the ion trap detector).

7.4.21 Metals in Ambient Air

The presence metals in ambient air will be determined using EPA Method PM-10. This method uses high volume air samplers (hivols) and the appropriate choice of filter media (i.e., Whatman binderless quartz filters and minimal metal background). The technique entails initially weighing clean/condition filters; installing the filter into calibrated hivols; drawing ambient air through the filter at a known flow rate for a twenty-four hours (typically, 60 cubic feet per minute (CFM); removing the dirty filter and re-weighing it, under the same conditions as initially weighed, thereby enabling the determination of total suspended particulate matter (TSP or PM10, depending upon the hivol sampling head); acid-digesting the entire filter, or portion of the filter; and subsequent analysis of the digestate for TAL metals by ICP.

7.4.22 PCB in Ambient Air

The presence of PCBs in ambient air will be determined using EPA Method TO-4. This method uses a modified high volume air sample which utilizes a glass fiber filter with a polyurethane foam (PUF) backup absorbent cartridge as a collection media. Sampling procedures are similar to those used for hivol collection of metals and particulates. The filter and PUF cartridge are extracted with 5% hexane in a Soxhlet extraction apparatus, the extracts are then reduced in volume using Kuderna-Danish (K-D) concentration techniques, the K-D concentrate is subjected to column clean-up, and the PCBs analyzed using gas chromatography with electron capture detection (GC-ECD) as specified in U.S. EPA Method 608 or other equivalent methods. Detection limits of greater than one nanogram per cubic meter (> 1 ng/m^3) are achievable when samples are collected at a flow rate of 200-280 liters/minute for twenty-four hours.

7.4.23 Sediment and Surface Water Bioassays

Aquatic toxicity tests will be conducted with sediment and surface water samples. Sediment and surface water tests will be conducted with samples as received, and sediment elutriates will be formulated at the laboratory from sediment and laboratory dilution water.

Surface water toxicity tests will be conducted for 7 days with fathead minnows, *Pimephales promelas*, and the water flea, *Ceriodaphnia dubia*. A screening test will be conducted as soon as water samples arrive at the laboratory to determine the

approximate toxicity. If no acute toxicity is detected, the definitive tests will be conducted only with full-strength water samples to verify the lack of chronic toxicity. If toxicity is suspected as a result of the screening tests, the definitive tests will be conducted with 5 concentrations of water that bracket the anticipated concentration where no effect will be observed. The 7-day tests will be conducted according to current EPA short term methods for estimating chronic toxicity of effluents and receiving waters to freshwater organism. detailed testing methods will be presented in a study protocol that will be prepared after discussion with Arthur D. Little and/or regulatory agencies.

Sediment toxicity tests will be conducted for 10 days with the amphipod *Hyalella azteca*, and for 7-14 days with either the midge *Chironomus tentans* or *Chironomus riparius* or the tadpole *Rana pipiens*. The definitive tests will be conducted only with full-strength sediment samples. The tests will be conducted according to current EPA sediment testing methods for freshwater organism.

For wastes containing greater than 0.5 percent solids, the liquid (if any) is separated from the solid phase and stored for later analysis. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase for 18 hours. Following extraction, the liquid extract is separated from the solid phase by filtration as described above.

7.5 Field Analytical Methods

Field screening measurements will also be collected using portable equipment in order to provide real-time data to assist in the optimization of the field sampling activities and for health and safety purposes. Field measurements such as pH, temperature, conductivity, and volatile organics in air, (using a photoionization detector) will be obtained. The quality of these data is generally comparable to EPA Level I (*Data Quality Objectives for Remedial Response Activities*, USEPA, EPA/540/G-87/003, dated March 1987).

Conductivity is measured by using a self-contained conductivity meter. It measures the ability of a water sample to carry an electric current in accordance with SOP ADL-5011 and EPA Method 120.1. For this project, a single instrument will provide the pH and temperature measurements as specified in SOP ADL-5013 in accordance with methods EPA 150.1 and EPA 170.1, respectively. The pH is determined electrometrically using a gas electrode in combination with a reference potential. In addition, this instrument will measure the temperature with a thermometer that is incorporated in the probe. Turbidity analysis is the comparison of the intensity of light scattered by a standard reference suspension under the same conditions. For this

project, a portable turbidimeter will be used as specified in SOP ADL-5026 and in accordance with method EPA 180.1.

A field laboratory will also be installed at the site to obtain screening requirements. This data will provide real-time data to assist in the optimization of the field sampling activities. The quality of the data generated at the field laboratory will be at Level II as defined by the EPA. We will use suitable calibration standards, reference materials, and sample preparation equipment to ensure meeting the quality objectives. Field screening measurements will also be collected using portable equipment to assist in the field effort and for health and safety purposes.

7.5.1 Total Petroleum Hydrocarbons by Non-Dispersive Infrared Spectrometry (NDIR)

To measure organic hydrocarbons in soil and water an NDIR analysis will be performed using a Horiba OCMA-220 Oil Content Analyzer. The NDIR field analysis for TPHC will be performed according to procedures provided by the instrument manufacturer, Horiba, and SOP ADL-2831, and by following the procedures equivalent to those of EPA Method 418.1, Total Recoverable Petroleum Hydrocarbons. Based upon specifications by Horiba, the instrument detection limit for the OCMA-220 infrared spectrophotometer is 0.1 mg/L for water and 0.3 mg/kg for soil. Based upon the results of a method detection limit study and the action level for this task, the practical quantitation limits will be 10 mg/kg for soil and 5 mg/L for water.

7.5.2 BTEX (Benzene, Toluene, Ethylbenzene and Xylene)

The method used for the determination of BTEX is based on method SW846-8020 and modified to be performed by direct injection into a gas chromatograph with a photoionization detector (GC/PID). A 5 gram aliquot of the soil sample is sonicated for 20 minutes after adding 5 mL of pentane, 0.5 grams of sodium sulfate and a spike solution. A 2 µL aliquot is then injected into the GC/PID system that consists of an HNU 311 GC with an MXT-1 column. A standard calibration is run containing the BTEX compounds at three concentrations, 1 ppm, 5 ppm and 20 ppm. Relative response factors are then calculated, subsequently the sample concentrations are determined with this information. For each batch, a procedural blank, a matrix spike, and a duplicate are processed.

7.5.3 PCBs using Immunosorbent Assay (Immunoassay)

The Enzyme Linked Immunoassay technique that will be used for the screening of soil samples for the presence of PCBs, is based on Draft Method SW-846 4030. Immunoassay is a technology recognized by the EPA as a valuable field screening tool. In general, the method is performed by adding an enzyme conjugate to a soil sample extract. This is then added to immobilized antibodies specific to PCB contained in test tubes. The antibodies linked to latex particles in the test tube, capture any PCB molecules present which are then collected in the surface of the test

tube. A color developing solution is then added, and the presence (or absence) of PCB can be measured with a reflectometer for semiquantitative results. The test is interpreted by comparing the response produced by testing a sample to the response produced by testing standards simultaneously. The working range for the field test kit that will be used for this task, is from 0.5 to 50 mg/kg for soils.

7.5.4 TNT Explosives using Immunosorbent Assay (Immunoassay)

The Enzyme Linked Immunoassay technique that will be used for the screening of soil and aqueous samples for the presence of TNT explosives, is based on Draft Method SW-846 4030. Essentially, this technique is the same as the one to be used for the field screening of PCBs. In general, the method is performed by adding an enzyme conjugate to the sample, or an extract in the case of a soil sample. Antibodies specific to TNT are linked to solid particles. TNT molecules present in the sample are captured by these solid particles and collected on the membrane surface of the collection device. A color developing solution is then added and the presence (or absence) of TNT can be semiquantitated with a reflectometer. The working range for the field test kit that will be used for this task, is from 0.2 to 2 mg/kg for soils and from 3 to 45 µg/L for aqueous samples.

8.0 Data Reduction, Validation, and Reporting

8.1 Arthur D. Little's Data Management

Data management for Fort Devens investigations refers to the effective management of all project related information; map, geotechnical and chemical data. Arthur D. Little's and the subcontracted laboratory's data management systems will be integrated in order to achieve an efficient flow of information from the laboratory to Arthur D. Little to USAEC.

8.1.1 Flow of Map Data into the IRDMIS

The IRDMIS map data entry refers to registering sampling locations by a specific convention and a coordinate system using a USAEC software program called PC IRDMIS or PC TOOL. Arthur D. Little will acquire the latest Fort Devens map data base from Potomac Research, Inc. (PRI) and will send this map database to the subcontracted laboratory so that proper record and group checks will be possible. Arthur D. Little will also be responsible for providing both the subcontracted laboratory and USAEC with updated map files based on sampling efforts at Fort Devens. When a new site is being sampled, Arthur D. Little will enter the map data to insure proper processing of the associated analytical data.

8.1.2 Flow of Geotechnical Data into the IRDMIS

Arthur D. Little will provide USAEC with updated geotechnical files based on sampling efforts at Fort Devens. The geotechnical data from new well sites will be processed and entered into the IRDMIS by Arthur D. Little. These data will be transferred into an ASCII-based "transfer" file which will be sent to PRI for processing, validation, and loading to the USAEC legal repository known as Level 3.

8.1.3 Flow of Chemical Data into the IRDMIS

Arthur D. Little will be responsible for the final review of ten percent of the analytical data associated with the sampling efforts at Fort Devens. This review is in addition, but identical to, the checks that are to be performed by the Arthur D. Little subcontracted laboratory. After the laboratory has analyzed Fort Devens field samples and created the IRDMIS transfer file, data files will be sent to Arthur D. Little for review. After this review, data will be submitted to PRI for eventual Level 3 status. This transfer will be confirmed as indicated by the USAEC weekly status report for each lot. Arthur D. Little's internal tracking system will also insure that all field samples have had the proper analysis performed and will contact the laboratory and the USAEC Project Officer whenever and wherever discrepancies arise.

8.2 Data Reduction

All the processes which change either the form of expression or quantity of data values or numbers of data items are part of the data reduction process.

Raw data from quantitative analysis procedures such as Gas Chromatography (GC), Gas Chromatography/Mass Spectrometry (GC/MS), High Performance Liquid Chromatography (HPLC), Inductively Coupled Argon Plasma (ICAP) and Ion Chromatography (IC) generally consist of peak areas (or peak heights) for the analytes of concern, internal standards, and surrogates. This applies to Class 1, 1A and TPH/GC-FID (a non USAEC approved method). These raw data will be converted to concentrations by use of calibration curves or relative response factors that relate peak area to the quantity of analyte introduced in the instrument. For field methods, the calibration procedures are generally less rigorous than those for Class 1 and 1A.

Generally data have been collected during the analysis of samples either into computer based data files or onto hard copy sheets, which, in turn, are either machine generated or hand written. In reporting results, rounding to the correct number of significant figures (this varies with the method) will occur only after all calculations and manipulations are completed. For dilutions, the number of significant figures will be reduced by one. Each analytical method referenced in Table 7-1 will describe the data reduction procedures for laboratory analysis results. In addition, they describe the correct procedure for using method blank results.

All uncorrected values less than the certified reporting limit, including no response, will be reported as "less than" the reporting limit. Results of the analyses will be entered into the USAEC IRDMIS as outlined in the IR Data Management User's Guide (USATHAMA September 1992). Non-certified analytes will be reported using detection limits documented in the appropriate method and will be flagged for data entry into the IRDMIS NTAM database.

8.3 Data Validation

Data Validation is an integral part of this QA program. USAEC data validation will be performed on one hundred percent of all data packages by the DataChem QA Coordinator. This is internal laboratory data validation and is not equivalent to EPA Region I functional guidelines for data validation. Even though the primary responsibility for this review and validation rests with the laboratory performing the analyses, the Arthur D. Little Lead Chemist, or designee, will be responsible for reviewing 10 percent of the data packages, following USAEC guidelines for data

review which are the same procedures followed by Datachem. See Section 8.1 - Arthur D. Little's Data Management.

The following is a brief outline of the data review and validation process:

- Evaluate for completeness of laboratory data;
- Evaluate data with respect to reporting limits;
- Evaluate data with respect to control limits;
- Review holding time data;
- Correlate laboratory data from related laboratory tests;
- Examine chain-of-custody records to ensure that custody was properly maintained;
- Compare data on instrument print-outs with data recorded on worksheets or in notebooks;
- Check to ensure that the same calibration was used for all samples within a lot;
- Examine chromatographic outputs and documentation of the reasons for manual integrations;
- Compare standard and sample preparation and injection records with instrument output to ensure that each output is associated with the correct sample;
- Examine calibration and tuning results to ensure that requirements are met;
- Check calculations on selected samples to ensure correctness;
- Check that GC/MS library searches have been performed for all unknowns, as required, and that the results have been evaluated and recorded;
- Examine all papers and notebooks to ensure that all pages are initialed, dated, and have sufficient explanation for the changes, and that all items are legible; and
- Compare transfer file, record, and group check results with analysis results.

8.3.1 USAEC Data Validation Procedures

The data processed through the DataChem Data Management System, where automated QC checks are performed, are reviewed by the analyst supervisor and analytical task manager. The data package containing the computerized reports and all raw data are completed and submitted with the data package to the QA supervisor. See Appendix B for checklist used in the data package review.

The project QA Coordinator or assistant, is responsible for reviewing and approving all data packets before submittal of data to Arthur D. Little. Data validation involves a thorough review of all data documentation from the raw data to the reported results contained in the lot folders. Data are considered complete only after they are approved by the QA staff prior to submittal. The reviews are performed on every batch to ensure that all QC checks required by the method are included in the batch.

With the use of the USAEC Data Review Checklist (see Appendix B), a through-package audit is performed. This includes checking the control charts, method blanks, standard matrix and sample matrix spike recoveries, surrogate recoveries, calibration curves, certified reporting limits, and units. The lab QA Coordinator or assistant makes an initial judgment on the acceptability of method blank and other data. Also included in the reviews are analyst's notebook pages, number of samples and sample identifications, dilutions, percent moisture, sample weights, chain-of-custody forms, standard preparation notebooks, instrument logbooks, etc. After ensuring that all these items are present and complete, the QA staff proceeds to review the raw data for precision, accuracy, and completeness. The raw data are checked against the reported values,and the appropriate calculations are spot checked.

Any discrepancies pertaining to any of the previously mentioned QA/QC checks are directed to the analytical task manager for verification, clarification, and/or correction, if necessary. Other queries regarding the data transmission file (e.g., improper method codes or incomplete field data) are addressed directly to Data Management. The questions are usually written under the "Comments" section of the USAEC Data Review Checklist (see Appendix B) or on separate supplements. Once the questions are satisfactorily answered, the QA staff initials and dates the batch and appropriate sections. The batch folder is then returned to Data Management for entry into IRDMIS.

The control charts are reviewed and transmitted to USAEC and Arthur D. Little weekly by the laboratory QA Supervisor. The control charts are reviewed by the laboratory coordinator, analytical task manager, and laboratory QA staff before any data are transmitted to USAEC IRDMIS data files.

Three data levels are used to indicate increasing QA and validation performed on the data. Data produced by the analytical laboratory and transmitted to USAEC IRDMIS are considered to be Level 1 data. At USAEC, Potomac Research, Inc. (PRI) loads the data into a computer for group and record checks. Errors, if present, are reported to the USAEC COR and chemist. Based on the nature of the error, the data are corrected or rejected. When the data have successfully passed group and record checks, they are elevated to Level 2. Level 2 data become Level 3 when they are uploaded into the USAEC pyramid mini-computer system. Level 3 data are available

to Arthur D. Little to create reports and graphs, but they cannot be changed by contractors. Generally, only Level 3 data are available to the USAEC COR. Under unique circumstances, the COR may request and receive Level 1 data. Level 1 data are used for information purposes only. Major decisions and risk assessments are based on Level 3 data only.

8.3.2 USEPA Data Validation Procedures

Approximately 10 percent of the analytical data packages generated in support of this program will be validated according to procedures defined in the U.S. Environmental Protection Agency National Functional Guidelines for Data Validation, as modified by Region I. This validation procedure is typically used to validate analytical data generated using EPA Contract Laboratory Program procedures. Due to differences in the analytical procedures and quality control associated with the USAEC program, it may not be possible to address all requirements of the EPA data validation procedures. The EPA data validation procedures address all of the issues listed in Subsection 8.3, using a series of worksheets.

The results of the data validation will be summarized in a memorandum, using the format prescribed by Region I.

8.4 IRDMIS Record and Group Checks

After each data packet has been reviewed by key individuals and validated by QA and data management staff, the data file from the packet is loaded into the USAEC IRDMIS systems at DataChem and run through the first record check and then the group check. Every data point is checked using these two routines. IRDMIS record check determines the following:

- Whether file names (such as CGW, CSW) and site type (BORE, WELL) combinations are valid;
- Validity of sampling program and technique, and existence or absence of depth measurement;
- Sample date, preparation/extraction date, and analysis date are compared to determine any holding-time violations;
- All test names are verified as valid, and either certified or flagged as not certified, at the time of analysis or at present;
- Value compliance with Certified Reporting Limit and Upper Certified Limit;

- Correct Boolean values, such as ND, LT;
- Correct QC test, mantissa and exponent values, and uncorrected mantissa and exponent values;
- If required, dilution mantissa, exponent, and moisture content inclusion; and
- Whether all required flagging codes are included.

IRDMIS group check determines the following:

- That all test names/analytes found in QC are present in all of the samples; and
- That all required QC spikes exist, all spiking levels are valid as determined by the methods table, and no aberrations exist in QC or sample data.

Specific criteria for record checks are based on the specific analytical method and on the current certification status of the laboratory performing the analysis. These criteria are stored in IRDMIS as certifications tables.

If any errors are found in group and record check which are not addressed on the Data Review Checklist by the laboratory analysts, laboratory project coordinator, or the QA Coordinator, the lot is returned to the laboratory project coordinator, so that the problem can be rectified. if changes to the analytical data are required, the lot is then resubmitted for QA review and, after re-validation, it is again processed through IRDMIS to ensure that any errors have been corrected.

After the data in a lot have successfully passed QA validation and IRDMIS record check and group check a transfer file of the lot is created and sent to USAEC via modem. The data are again run through record and group check by USAEC, and after passing the data checks, are elevated to Level 2.

8.5 Data Reporting

The results for samples analyzed for USAEC projects are entered into the USAEC-provided software program (IRDMIS) by the subcontracted laboratory. Data created using the IRDMIS can then be electronically transmitted to Arthur D. Little's Data Manager or a diskette together with hard copy printouts can be submitted.

All the subcontracted laboratory data are entered on a coding form by the analyst, which is verified by the peer checker and, group leader/section manager. Laboratory

QA personnel review data for obvious errors. These data are encoded onto a diskette, checked through two USAEC software routines, then printed out and verified by visual inspection by a Data Entry Specialist. Verified analytical results are then submitted to Arthur D. Little. DataChem retains a duplicate diskette of all data submitted. This sequence of data management activities is shown in Figure 8-1.

All information pertaining to the analysis of a lot of samples is collected into a data package at the completion of analysis. The contents of data packages varies with methods of analysis. The package is reviewed by the Laboratory Quality Assurance to eliminate technical errors that might affect the litigation quality of the data. The reported data is also reviewed by Data Entry for completeness before release.

The subcontracted laboratory subsequently sends data packages to Arthur D. Little for final review (10% of all data packages). Subsequent to the final review, all pertinent documentation in appropriately-labeled boxes is delivered to USAEC.

9.0 Internal QC Checks and Frequency

9.1 Control Samples

Control samples are those that are introduced into the train of environmental samples to function as monitors of the analytical method. All required QC samples will be prepared from standard matrices or actual field samples and processed through the complete certified analytical method. Stock solutions used to spike QC samples will be prepared independently of stocks used for calibration or certification samples.

9.2 Field Control Samples

Various types of field QC samples are used to check the cleanliness and effectiveness of field handling methods. Field QC samples help indicate whether project data quality objectives have been met by providing quantitative and qualitative measures of precision, accuracy, representativeness, completeness, and comparability parameters. They are analyzed in the laboratory as samples, and their purpose is to assess the sampling and transport procedures as possible sources of sample contamination and document overall sampling and analytical precision. Field staff may add blanks or duplicates if field circumstances are such that they consider normal procedures insufficient to prevent or control sample contamination, or at the direction of the Task Manager. Rigorous documentation of all field QC samples in the site logbooks is mandatory.

Field QC samples and the programmatic recommendations for frequency of collection are briefly described below. The specification and number of field QC samples to be collected during specific Delivery Orders are provided in the supplements.

9.2.1 Trip Blanks

Trip blanks are not exposed to field conditions; results from the analysis of trip blanks are used to assess potential contamination from everything except ambient field conditions. Trip blanks are prepared at the laboratory prior to the sampling event by adding deionized water to a 40-ml VOA vial containing two to three drops of concentrated hydrochloric acid; they are shipped with the sample bottles. One trip blank will be used with every shipment of water samples for volatile organic analysis or at a frequency of one per 20 samples, which ever is greater. Each trip blank will be transported to the sampling location, handled in the same manner as a field sample (except the bottlecap is not removed), and returned to the laboratory for analysis without having been opened in the field.

9.2.2 Field Equipment/Rinsate Blanks

The results of analyzing field equipment/rinsate blanks are used to document that sampling equipment have been properly prepared and cleaned before field use and that cleaning procedures between samples are sufficient to minimize cross-contamination. Rinsate blanks are prepared on-site by passing analyte-free water over sampling equipment; they are analyzed for all applicable parameters. If a sampling team is familiar with a particular site, it may be possible to predict the areas or samples that are likely to have the highest concentration of contaminants. The equipment blank sample should be collected after a sample is expected to exhibit high concentrations of target analytes.

For dissolved metals analysis in water samples, equipment blanks will be collected by passing analyte-free water over the filtration apparatus. These blanks will be collected at a frequency of one per day, per filtration apparatus used.

Rinsate blanks are collected at a frequency of one per day per equipment type for each matrix, whichever is greater. Rinsate blanks will not be collected for sampling activities using dedicated equipment to collect each sample.

9.2.3 Field Duplicates

Field Duplicates are two samples collected independently at a sampling location during a single sampling event. The results of analyzing field duplicates are used to assess the consistency of the overall sampling and analytical system. Field duplicate samples are generally collected at a rate of one per 20 or fewer samples per matrix.

9.2.4 Field Blanks

Field Blanks are exposed to field conditions by preparing the blanks at the sample collection site. Field Blanks are collected at a rate of one per 20 field samples for each matrix.

9.3 Laboratory Control Samples

QC data are necessary to determine precision and accuracy and to provide quantitative evidence that the method is performing comparably or better than when documented during method development and certification. Laboratory-based control samples will consist of standards, surrogates, spikes, and blanks. Data generated from control samples which are included in each lot will be plotted on control charts to monitor day-to-day variations in routine analyses. For this program DataChem will follow the approach described by the *USATHAMA Quality Assurance Program* for approved methods with respect to laboratory control samples. For non-USAEC methods will follow the specific method directives. Generally, a blank, a spike, and a duplicate will be included in each lot of 20 or fewer samples.

The types of laboratory control samples and the minimum acceptable performance for non-USAEC methods for USAEC projects are briefly described below.

9.3.1 Laboratory Blanks

In addition to field blank samples, three types of blanks that may be analyzed in the laboratory are calibration blanks, method blanks, and reagent blanks. method blanks and reagent blanks are used to assess laboratory procedures as possible sources of sample contamination. Calibration blanks establish the analytical baseline against which all other blanks are measured.

- Method Blanks are laboratory blanks that correspond to the first step in sample preparation and as such, provide a check on contamination resulting from sample preparation and measurement activities. For USAEC-approved methods, method blanks for water and soil samples consist of a standard matrix that is subjected to the entire sample procedure as appropriate for the analytical method being utilized. For non-USAEC methods, the method blank is typically an appropriate volume laboratory water carried through the entire preparation and analysis procedure.

- Reagent/Solvent Blanks are closely related to method blanks, but they do not incorporate all sample preparation materials and analytical reagents in one sample. When a method blank reveals significant contamination, one or more reagent blanks may be prepared and analyzed to identify the source of contamination.

- Calibration Blanks consist of pure reagent matrix and are used to zero an instrument's response to the level of analytes in the pure reagent matrix. They do not provide a direct indication of the types, sources, or levels of contamination, but they establish the analytical baseline.

9.3.2 Laboratory Duplicates

Laboratory duplicate samples are defined as two sample aliquots taken from the same sample container and analyzed independently. The results of these analyses serve as an indicator of the precision of the method and the sample results. The frequency of these duplicates is specified in the approved methods. For non-USAEC methods, duplicates will be prepared with the frequency specified in the referenced method.

9.3.3 Calibration Standards

A calibration standard is prepared in the laboratory by dissolving a known amount of a pure compound in an appropriate matrix. The final concentration calculated from the known quantities is the true value of the standard. The results obtained from these standards are used to generate a standard curve and thereby quantify the compound in the environmental sample. See Section 7.0 for calibration procedures.

9.3.4 Spike Sample

A sample spike is prepared by adding to an environmental sample or standard matrix (for USAEC approved methods; before extraction or digestion), a known amount of pure compound of the same type that is to be assayed for in the analysis. The spike may also be a surrogate compound for the analyte of interest. These spikes simulate the background and interferences found in the actual samples and provide a mechanism to verify overall method performance. The calculated percent recovery of the spike is taken as a measure of the accuracy of the total analytical method. For USAEC approved methods, between one and three spiked samples, as specified in each method, will be included in each lot. For non-USAEC methods, spiked samples will be analyzed with the frequency specified in the method.

9.3.5 Internal Standard

An internal standard is prepared by adding a known amount of pure compound to the environmental sample; the compound selected is not one expected to be found in the sample, but is similar in nature to the compound of interest. Internal standards are added to the environmental sample just prior to analysis.

9.4 Concentration and Frequency of Control Samples

One method blank shall be included in each analytical lot, regardless of certification class. A single method blank/spike for GC/MS procedures (Class 1A) serves as a standard matrix QC blank and spike. The frequency of QA samples is summarized in Table 9-1. The following spiked QC samples will be included in each analytical lot:

9.4.1 Class 1 Approved Method

- Two independently-prepared spiked standard matrix QC samples shall contain all the control analytes at a concentration near the upper end of the certified range or approximately ten times certified reporting limit (CRL).

- One spiked standard matrix QC sample prepared at the regulatory action level or approximately two times certified reporting limit.

Control analytes will be specified in USAEC approved methods. For multi-analyte methods, USAEC will designate the required control analytes. Control limits will be initialized for all analytes.

Control charts will be maintained for each control analyte. Out-of-control situations are discussed in Section 12.

Table 9-1: Frequency of Laboratory QC Samples for USAEC Performance Demonstrated Methods

USAEC CLASS	ANALYSES	QC SAMPLES FREQUENCY/LOT	
		Method Blank	Spikes
1	Metals	1	3
	Explosives	1	3
	Nitrate	1	3
	Pesticides/PCBs	1	3
	Sulfate	1	3
	Chloride	1	3
	Organophosphorus Pesticides	1	3
	Herbicides	1	3
	Phosphate	1	3
	TKN	1	3
1A	VOAs	1*	1
	BNAs	1*	1
2	Pesticides/PCBs (Confirmation)	1	1

* = Surrogates only

9.4.2 Class 1A Approved Method (GC/MS only)

- One independently-prepared standard matrix QC sample (method blank/spike), containing all the certified surrogate analytes at approximately ten times certified reporting limit (not to exceed the upper limit of the certified range). For the method blank/spike, surrogate results represent the QC spike, while unspiked, non-surrogate results represent the method blank.

- Every field sample will be spiked with certified surrogate analytes at approximately ten times certified reporting limit. The spike concentration will be the same for all the samples.

Control analytes will be specified in the USAEC standardized method. Additional non-surrogate target analytes may be specified by the USAEC project officer.

Control charts will be maintained for each control analyte. Out-of-control situations are discussed in Section 12.

Results of natural matrix surrogate spikes are reported to the IRDMIS. Appropriate flagging codes will be used to indicate any problems with surrogate recoveries.

9.5 Data Reporting for QC

9.5.1 Class 1, Class 1A, and Class 1B Approved Methods

Results for each analyte in the spiked QC sample will be determined using the same acceptable calibration curve that is used for analytical samples in the lot. Raw values below the CRL will be reported as "less than" the reporting limit. All certified data will be entered into the IRDMIS by personnel trained in the use of the IRDMIS.

The results for the method blank and spiked QC samples will be quantified each day of analysis. A new lot of samples will not be introduced into the analytical instrument until the results for QC samples in the previous lot have been calculated, plotted on control charts, and the entire analytical method has been shown to be in control.

Data from the method blank will be reported, usually as "less than" the CRL for each analyte. Any values above the terms of concentration, will be entered into the IRDMIS. Data collected from analyses with contaminated blanks will not be used or will be reported flagged.

10.0 Performance and System Audits

Performance audits are a quantitative evaluation of a measurement system and generally consist of evaluation of a laboratory's performance in analyzing performance evaluation samples and blind samples. DataChem Laboratories has participated in performance audits by USAEC and has also participated in EPA's water pollution and water supply performance evaluation program.

System audits are a qualitative on-site review and evaluation of the components and implementation of USAEC's QA Program (January 1990). They consist of field, laboratory, and project audits that are performed by qualified personnel from the Arthur D. Little QA or technical staff or from external regulatory agencies.

The Quality Assurance reviews under this subtask are systematic evaluations of four aspects of the Fort Devens project: (1) the field/geotechnical activities, (2) the laboratory analysis activities, (3) data files and packages, and (4) overall project activities and document. The field Quality Assurance reviews will be undertaken by the Arthur D. Little Program QA Officer or his designee. The laboratory Quality Assurance reviews will largely be undertaken by our subcontracted laboratory, with QA oversight provided by the Arthur D. Little Lead Chemist or her designee. The Arthur D. Little Lead Chemist will also review IRDMIS data files and USAEC data packages from our subcontracted laboratory prior to sending files and packages to USAEC. These reviews will assure that activities and data are implemented in accordance with this Work Plan and the QAPjP and associated Standard Operating Procedures, provided as a separate document. These documents adhere to the requirements specified in the *USATHAMA QA Program*, and the *USATHAMA Geotechnical Requirements for Drilling, Monitoring Wells, Data Acquisition, and Reports*.

10.1 Field Audits

Field audits are performed randomly on a variety of projects to determine the accuracy of the field sampling, documentation, and measurement systems. A schedule for field audits for the Fort Devens field sampling effort will be determined by the Arthur D. Little Task Manager or the Project QA Officer, and USAEC.

Field Quality Assurance reviews will be performed on site for one day during field investigation activities. The reviews will be conducted by the Project Quality Assurance Officer or his designee. Through a combination of on-site observations and on-site and off-site review of documentation, the following will be reviewed to ensure conformance with the above referenced documents:

- Field logbooks and forms,
- Field chemical/physical analyses including calibration and QC samples,
- Containers and sample preservation used for collected samples,
- Sample storage and security,
- Sample containers,
- Location and elevation survey,
- On-site steam cleaning drill rig procedures prior to drilling activities, between each well, and before leaving the site,
- "Dig-safe" and UXO screening procedures,
- Confinement and containerization of drilling wastes (waste steam cleaning condensates from drill rigs and the PVC pipe used for casings; drilling fluid, if used; surface runoff, and antifreeze if used),
- Drilling activities (water sources used) and well materials (Ottawa sand, bentonite and grout),
- Well development and presample purging techniques,
- Depth measuring techniques,
- Well construction and security,
- Accurate drawings and notes of the well's location and drilling operations,
- Specified numbers and types of soil, ground water, surface water, and sediment samples are collected and sent to the laboratory, and
- Custody forms, including sample labels and chain-of-custody records.

The Field Checklist provided in Appendix W of the *USATHAMA Quality Assurance Program*, PAM-11-4, will be used during this audit. External audits may also be performed by a representative of the USAEC Chemistry Branch.

10.2 Laboratory Audits

A system internal audit by the DataChem Laboratories Project Manager and QA Coordinator (or designees) is made before any new experimental procedures are implemented. Systems audits are also made for critical functions during the sampling and analysis program. The system audit is of a qualitative nature and consists of an on-site review of the laboratory's QA system and physical facilities for sampling, calibration, and measurement. The results of these reviews will be documented in initial and final laboratory visit checklists.

Critical functions will be audited by the DataChem QA Coordinator to verify that:

- Standards, procedures, records, charts, floppy disks, and notebooks are properly maintained;
- Actual procedures agree with written instructions; and
- QA records are adequately filed and maintained to assure protection and retrievability.

The QA Coordinator or assistant will also assess the results of QC sample analyses.

In addition to internal laboratory audits, USAEC will perform external audits. Currently, DataChem Laboratories is audited by USAEC every six months by representatives of the USAEC Chemistry Branch.

Findings from DataChem audits will be documented in a bound notebook and maintained in a Project QA file. Findings will include observations and notations as to whether approved practices are followed. A summary of findings will be distributed to the DataChem Laboratories Corporate QA Officer, the Project Manager, Analytical Coordinator, Arthur D. Little Task Manager and Lead Chemist, and USAEC.

10.2.1 Data Review

As required by the USATHAMA QA Plan, all data packages will be reviewed by the DataChem Quality Assurance Coordinator. This review serves two purposes; it ensures that all required data and documentation are provided in the package and it checks the content for technical and recordkeeping errors. The reviewer's name and date of review will be recorded on the QAC Checklist, any corrective actions required will also be noted. When the corrective action has been completed the QAC will initial and date the original comment. The QAC's signature on the checklist will indicate that the data are considered valid and usable.

Our subcontracted laboratory will provide Arthur D. Little with USAEC data packages and IRDMIS data files. We will review data packages and files and transfer reviewed files to IRDMIS.

An additional review of approximately ten percent of the data packages will be performed by the Arthur D. Little Lead Chemist or designee. The packages will be chosen to cover as broad as possible a range of analyses and matrices. In some cases, a particular lot may be selected for additional review by the Arthur D. Little or USAEC Project Manager. The Lead Chemist will assess the completeness of the documentation provided, adherence to the certified or other published method, adherence to USAEC quality control requirements and acceptability of the quality control data. The Lead Chemist will also provide a technical review of the data and verify at least one calculation for standard preparation and final reported analyte values from the raw data contained in the data packages to the final reported value on the IRDMIS. Any discrepancies or omissions will be discussed promptly with DataChem. A copy of the Arthur D. Little Lead Chemist's review will be added to the data package.

At least ten percent of the analytical lots on IRDMIS data files will be record-checked to assess if the method was performed correctly and within the sample holding times specified. After successfully passing the record check, the samples are group-checked to confirm that the proper number of control samples were analyzed and each sample site corresponds to a valid map site. After successful record and group checks, data may be transferred to PRI over the 3COM network.

Any deviations or problems with data files and/or packages will be reviewed with the subcontractor laboratory, and appropriate corrective actions will be taken as necessary and will be fully documented.

10.3 Project Audits

Project audits may also be performed on files containing relevant project documentation. These audits will be triggered by apparent non-conformance to the *USATHAMA Quality Assurance Program* and/or in response to corrective actions. Project files are evaluated against internal document control SOPS. Project audits are performed on a random percentage of projects by the Arthur D. Little Program QA Officer or his designee.

11.0 Preventive Maintenance

11.1 Field Instruments

All field instruments and equipment used for sample analysis will be serviced and maintained only by qualified personnel. All repairs, adjustments, routine maintenance, and calibrations will be documented in an appropriate logbook or data sheet that will be kept on file at the field equipment warehouse. The instrument maintenance logbooks will clearly document the date, the description of the problems, the corrective action taken, the result, and who performed the work. Arthur D. Little maintains a sufficient number of spare parts for all field instruments and, in many cases, back-up instrumentation to minimize downtime of instruments and delays in analyses.

11.2 Laboratory Equipment

The subcontracted laboratory, DataChem, maintains maintenance contracts with the major instrument manufacturers for 24-hour, seven day per week emergency call service. DCL performs routine maintenance to prevent instrument malfunction and minimize downtime, and to optimize instrument capabilities.

The schedule of preventative or routine maintenance checks are, in general, outlined within the specific equipment's operation manuals and in the analytical procedures performed. DataChem adheres to these schedules, and it is the responsibility of both the project analyst and management to monitor that these checks are completed. Figure 4-1 provides the SOP Reference for Instrumentation Maintenance for our subcontracted laboratory.

The laboratory maintains an inventory of replacement parts for all analytical instrumentation; this enables analysts to perform routine maintenance and repair of instruments as needed.

12.0 Procedures Used to Assess Data Accuracy, Precision, and Completeness

This section describes the statistical analysis of data obtained during analysis of Fort Devens samples by USAEC-approved methods. The calculations described in this section are contained in computer software developed by USAEC.

The statistical calculations compare the measured concentration of standards in spiked samples with the known spiked concentrations of these target analytes. The measured concentrations are determined from calibration curves constructed according to the standardized method. Recovery factors will be not be used to correct measured concentrations during analysis of the certification data. These calculations must be performed for each target analyte in a method.

12.1 Lack of Fit (LOF) and Zero Intercept (ZI) Tests

All data must be collected during periods when instrumental calibration was in control (i.e., within plus or minus 10 percent of the mean response for inorganics analyses in surface/ground waters and within plus or minus 25 percent of the mean response for all other analyses). Data obtained from valid methods using properly calibrated instruments are expected to be linear and have a zero intercept, when measured concentrations are compared to the target concentrations. This relationship must be tested because calculation of the CRL assumes that a linear relationship exists.

Data obtained during certification analyses shall be first examined for any outliers before being tested for linearity using the LOF and ZI tests. In the absence or replacement of an outlier, data from each of the certification analyses shall be pooled and tested for LOF.

12.2 Certified Reporting Limit (CRL)

Before any analytical system is employed in a survey, sufficient spikes and blanks will be run to statistically establish the lowest sample concentration to be reported. This concentration is the CRL. For USAEC projects, CRLs shall be determined by using the USAEC program with 95 percent confidence limits. This CRL is associated with the entire method and reflects all sample preparation and measurement steps.

The CRL is derived from the following assumptions:

- The relationship between the measured concentration and target concentration is linear;
- The variance about the least squares linear regression line is homogeneous over the tested concentration range; and
- Measured concentrations for a given target concentration are normally distributed.

Based on these assumptions, the least squares linear regression line, of the form indicated in Equation 1, can be determined. The certification performance data (X, Y paired data) are used to determine the slope and Y-intercept of the least squares regression line according to the formulae provided below in Equations 2 and 3; these equations assume that errors occur only in the measured concentration.

Equation (1)

$$Y = Y_o + bX$$

where:

Y = least squares best fit to found concentration;
Y_o = Y axis (found concentration) intercept;
b = slope of the line; and
X = target concentration.

Equation (2)

$$b = \frac{N \Sigma X_i Y_i - \Sigma X_i \Sigma Y_i}{N \Sigma X_i^2 - (\Sigma X_1)^2}$$

where:

N = number of data points;
X_i = the i-th target concentration; and
Y_i = the i-th found concentration.

Equation (3)

$$Y_o = \frac{\Sigma Y_i - b \Sigma X_i}{N}$$

where:

The equations for the upper confidence limit (Equation 4) and the lower confidence limit (Equation 5) about the regression line are provided below:

Equation (4)

$$Y_{UCL} = Y_o + bx + S_{Y.X}\, t \left[\frac{(1+1)}{N} + \frac{(X_i - \bar{X})^2}{\Sigma (X_i - X)^2} \right] 1/2$$

Equation (5)

$$Y_{LCL} = Y_o + bX - S_{Y.X}\, t \left[\frac{1}{N} + \frac{(X_i - \bar{X})^2}{\Sigma (X_i - X)^2} \right] 1/2$$

and $S_{y.x}$ is defined by Equation (6) below:

Equation (6)

$$Sy,\ x,\ s = \left[\frac{\Sigma (Y_i - [\bar{Y} + b(X_i - \bar{X})])^2}{N - 2} \right] 1/2$$

where:

t = Student's t-test for 2-tailed P = 0.10 and N - 2 degrees of freedom;
Y_{UCL} = Upper confidence limit; and
Y_{LCL} = Lower confidence limit.

$\overline{X}$ = the average of all target concentrations; and

$\overline{Y}$ = the average of all found concentrations.

The calculated reporting limit, X_d, is the value of X corresponding to a point on the lower confidence limit curve where the value of Y equals the value of Y on the upper confidence limit curve at X = 0. An example of the statistical analysis of reporting limit using the USAEC computer software is shown in the *USATHAMA Quality Assurance Program Manual* (January 1990).

The calculated reporting limit will be reported as the CRL of the method, provided that at least one of the tested concentrations is at or below the calculated reporting limit. Otherwise, the lowest tested concentration is the minimum level that can be reported as the CRL. The CRL will not be less than the lowest tested concentration.

The confidence limits provide an optimistic estimate of the method reporting limit because interferences found in natural samples will be absent. The highest tested concentration will represent the upper limit of reportable data. All sample measurements must be performed within the tested range. A calculated reporting limit higher than the highest target concentration indicates that either an invalid range was chosen or the method is not suitable for analysis of that compound.

12.3 Method Certification Accuracy

As calculated according to Section 12.2, the slope, b, of the least squares linear regression line of a plot of observed versus target concentrations is a measure of the accuracy of the method. A slope (accuracy) of "plus one" (1.00) indicates 100 percent recovery over the complete analytical method and tested range. Failure to consider the intercept, if it is significantly different from zero, could result in an erroneous estimate of the accuracy. If the intercept is significantly different from zero, then there is a need to investigate whether the blank was correctly applied or if there is some other systematic error in the system. At no time should the laboratory continue until this is investigated. Experimental values may deviate from this expected value. The certification data will provide an optimistic estimate of the method accuracy because interferences found in natural samples will be absent. The accuracy estimate for the complete certification data set is incorporated into the USAEC IRDMIS. The slope for the complete data set will be used to indicate the accuracy of the method.

12.4 Method Certification Standard Deviation

For all method certification, the standard deviation, s, will be calculated at each target concentration according Equation 7. The standard deviation provides an indication of the precision of the analysis. This calculation is performed by the USAEC software.

Equation (7)

$$S = \left[\frac{\Sigma Y_i^2 - \frac{(\Sigma Y_i)^2}{N}}{N - 1} \right]^{1/2}$$

where:

S = standard deviation;
Y_i = the measured concentration; and
N = total number of Y values at each target concentration.

12.5 Method Certification Percent Inaccuracy

For all method certification, the percent inaccuracy will be calculated at each target concentration according to Equation 8. This calculation is performed by the USAEC software.

Equation (8)

$$Percent\ inaccuracy = \frac{\bar{Y} - X}{X} (100)$$

where:

X = target concentration; and

$\bar{Y}$ = average measured concentration at the target concentration.

12.6 Method Certification Percent Imprecision

For all method certification, the percent imprecision will be calculated at each target concentration according to Equation 9. This calculation is performed by the USAEC software.

Equation (9)

$$\textit{Percent imprecision} = \frac{S}{\overline{Y}} (100)$$

where:

S = standard deviation; and

$\overline{Y}$ = average measured concentration at the particular target concentration.

12.7 Data Moving-Average Accuracy and Precision

Moving-average control charts will be maintained for the specified surrogates in the spiked standard matrix sample (Class 1A). The X - R three-point moving-average control chart will be constructed for each control analyte as follows:

- Use percent recovery to allow for minor variations in spiking concentrations;
- The first plotted point is the average of the first three recoveries (from certification, at concentrations nearest the spiking level);
- Subsequent points are obtained by averaging the three most recent individual recovery values (outliers excluded from calculation but not from plot);
- The range for each point is the difference between the highest and lowest value for each group of three values; and
- The central line, upper warning limit (UWL), upper control limit (UCL), lower warning limit (LWL), and lower control limit (LCL) for the control charts are calculated using the following formulas:

Equation (10)

$$Average = \overline{\overline{X}} = \frac{\Sigma \overline{X}}{K}$$

Equation (11)

$$Range\ \overline{R} = \frac{\Sigma R}{K}$$

where:

$\overline{\overline{X}}$ = between-group average of the average recovery of the three points (within group);

$\overline{X}$ = average within-group recovery for the three points;

R = within-group difference between recoveries for data pairs; and

K = cumulative number of pairs in the database.

Upper Warning Limit (UWL) on Average:

$$UWL_x = \overline{\overline{X}} + 0.682\ \overline{R}$$

Upper Control Limit (UCL) on Average:

$$UCL_x = \overline{\overline{X}} + 1.023\ \overline{R}$$

Lower Warning Limit (LWL) on Average:

$$LWL_x = \overline{\overline{X}} + 0.682\ \overline{R}$$

Lower Control Limit (LCL) on Average:

$$LCL_x = \overline{\overline{X}} + 1.023\ \overline{R}$$

Upper Warning Limit (UWL) on Range:

$$UWL_R = 2.050\ \bar{R}$$

Upper Control Limit (UCL) on Range:

$$UCL_R = 2.575\ \bar{R}$$

Lower Warning Limit (LWL) on Range:

$$LWL_R = 0$$

Lower Control Limit (LCL) on Range:

$$LCL_R = 0$$

All data will be plotted, regardless of whether the lot is in control. Plotted points represent averaged instrument measurements and not the individual measurement values. Each individual measurement value will be tested as an outlier using Dixon's test at the 98 percent confidence level (*USATHAMA Quality Assurance Program Manual* (January 1990), Appendix K). If the datum is not classified as an outlier by the test, the point will be included in updating the control chart limits. If an individual measurement is classified as an outlier, it will be used in calculating the three-point moving average for plotting purposes only; the measurement is then excluded from calculations based on the three most recent acceptable individual points that are used to determine moving-average and the control chart limits. Method control will be judged according to the criteria in Section 8.0.

After the first control chart points, control limits will be recalculated using only in-control data points. Any points falling outside of the control limits (UCL or LCL) will be dropped from the calculations (but left on the charts) and the control limits recalculated using only points between the UCL and LCL. Charts will then be updated with the newly calculated control limits and all points plotted.

Lots associated with points outside of the new control limits may require resampling and/or reanalysis as determined by USAEC COR on a case-by-case basis. These limits will then be used to control analysis of the next 20 lots. The control charts are now the outlier test, although individual measurements will continue to be tested as outliers if they appear not to be representative of the data set. A maximum of the 40 most recent lots will be used to recalculate control limits for 60 or more lots (40-point slide).

When, as a result of audits or QC sample analysis, sampling or analysis systems are shown to be unsatisfactory, a corrective action shall be implemented. The Laboratory QA Coordinator will be notified and the necessary corrective action taken.

12.8 Control Charts

For Class 1, Class 1A, and Class 1B approved methods, control charts are used to monitor the variations in the precision and accuracy of routine analyses and to detect trends in these variations. The construction of a control chart requires initial data to establish the mean and range of measurements. The QC control charts are constructed from data representing performance of the complete analytical method. Data used in control charts are not adjusted for accuracy. Control charts are not used with Class 2 approved methods.

Control charts include the analyte, method number, DataChem laboratory code of UB, spike concentration, and chart title. All data presented on a control chart are also presented in tabular form. The following charts may be selected from the USAEC-supplied computer control chart program:

1. Single-Day X-Bar Control Chart (High Spike Concentration)
2. Single-Day Range Control Chart (High Spike Concentration)
3. Three-Day X-Bar Control Chart (Low Spike Concentration)
4. Three-Day Range Control Chart (Low Spike Concentration

In addition, the following information is also included on each control chart:

- Three-letter lot designation for each point, shown on the X=axis;
- Percent recovery (for X-bar control charts), or range (for R control charts) along the Y-axis;
- Upper control limit (UCL);
- Upper warning limit (UWL);
- Mean;
- Lower warning limit (LWL), on X-bar charts; and
- Lower control limit (LCL), on X-bar charts.

For some analytes specified by USAEC, warning limits on X-bar charts are deleted and replaced by modified control limits based upon data quality specifications.

12.8.1 Control Chart Plotting: Single-Day

The initial control chart is prepared using the four days of certification data closest to the spiking concentration used during analysis. The average (X-bar), average range (R), and control limits for both are updated after each in-control lot for the first 20 lots. Limits established after lot 20 are used for the next 20 lots. Control charts are updated after each 20 lots thereafter, using the most recent 40 points. In interpreting the control charts developed for the initial lots (1-20), the limits established from the previous lots are used to control the current lot.

When modified limits are established, data for samples are accepted if the control data fall between the modified limits. If modified limits have not been established, data for samples are accepted, based upon the recoveries established during certification and the current performance of the method. In updating the control charts, the new data must be combined with the individual values of previous average percent recoveries and not the mean of all previous data. Only lots evaluated as in-control are applicable to the 20 and 40 lot requirements for establishing and updating control chart limits. Out-of-control or outlier points are plotted; however, such lots are not utilized in lot number requirements or control chart calculations.

All recoveries are plotted, whether or not the lot is in-control. Plotted points represent averaged instrument measurements are not the individual measurement values. Each individual recovery measurement value is tested as an outlier using Dixon's Test at the 98 percent confidence level. If the datum is not classified as an outlier, it is not used in updating the control chart limits. Range data are not subject to outlier testing.

After the first 20 in-control sample lots, control limits are recalculated using only in-control data points. The control limits are then drawn backward to encompass all previous points. Any points falling outside the control limits (UCL or LCL) are dropped from the calculations (but left on the charts) and the control limits recalculated using only points between those limits. This practice of dropping points and recalculating limits is performed only once, at the initialization of stable limits. Charts are then updated with newly calculated control limits and all points plotted.

12.8.2 Three-Point Moving Average

Analytical data for analytes prepared in the single low concentration QC sample are plotted and evaluated on a three-day-moving-average control chart. Data for the surrogates spiked in a standard matrix and used in GC/MS analyses are also charted on a three-day-moving-average control chart. Plotting criteria for the three-point moving average control charts are similar to those described above for single-day control charts. Data for analytes prepared in duplicate QC samples at high concentrations are plotted and evaluated on single-day control charts.

Computer generated control charts maintained by Quality Assurance are updated and printed weekly, while analysts plot data points by hand as sample lots are analyzed. This allows for both computer maintenance and evaluation of a large data base with software calculation of control limits, and immediate daily surveillance of analytical trends.

12.9 Out-of-Control Conditions

Results of the analysis of quality control samples are reported to QA within 48 hours of completion through the analyst's submission of a Preliminary QC Report.

The analyst quantifies each analyte in the method blank and spiked QC sample each data of analysis. Processing of additional lots will not occur until the results of the previous lots have been calculated, plotted on control charts as required, and the entire analytical method shown to be in control.

An indication of an out-of-control situation may include: a value outside the control limits or classified as outlier by statistical test; a series of seven successive points on the same side of the mean; a series of five successive points going in the same direction; a cyclical pattern of control values; or two consecutive points between the UWL and UCL or the LWL and LCL.

If the points for at least two-thirds of the control analytes for a multi-analyte method are classified as in-control, the method is in-control and environmental sample data may be reported. A method may be deemed out-of-control even if greater than or equal to 2/3 of the control analytes meet control criteria. Of the remaining control analytes (less than 1/3 possible out-of-control), if one analyte has two consecutive out-of-control points, as defined above, the method is deemed out-of-control. If data points for fewer than 2/3 of the control analytes are classified as in-control, the method is considered to be out-of-control and all work on that method must cease immediately. No data for environmental samples in that lot may be reported.

In all cases, investigation by the analyst and the Quality Assurance Coordinator is required to determine the cause of the condition and to decide on appropriate corrective action. The pertinent details of the situation and the corrective action taken are fully documented in a Corrective Action Report (CAR). (See also Section 10.0.) Field sample data effected by the situation are evaluated and reanalyzed as necessary.

When a method is determined to be out-of-control, the analysis of field samples by that method is suspended. Corrective action must be documented and the method must be demonstrated to be in-control before analysis of field samples is reinstated. Analytical control is demonstrated through the acceptable analysis of an appropriate set of QA samples.

12.10 Non-USAEC Methods

For non-USAEC methods, including laboratory tests for Total Suspended Solids (TSS) and Total Petroleum Hydrocarbons (TPHC), Total Organic Carbon (TOC), asbestos, hardness, alkalinity and field tests for pH, temperature, conductivity, turbidity, and total volatile organics (by photoionization detection), the QC samples and procedures for assessing data precision and accuracy are provided in the referenced method or Standard Operating Procedure.

12.11 Completeness

Completeness is a measure of the amount of usable data obtained from a measurement system compared to the total amount expected to be obtained. It is calculated as follows:

$$\textit{Completeness (\%)} = \frac{\textit{Number of valid analyses}}{\textit{Number of analyses requested}} \times 100$$

13.0 Corrective Actions

When, as a result of staff observations, audits or QC sample analysis, sampling or analysis systems are shown to be unsatisfactory, corrective action will be implemented. Staff and management at Arthur D. Little and/or DataChem may be involved in the corrective action. If previously reported data are affected by the situation requiring correction or if the corrective action will impact the project budget or schedule, the action will directly involve the Task Manager and the USAEC Project Officer. Corrective actions are of two kinds:

- Immediate - to correct or repair nonconforming equipment and systems. The need for such an action will most frequently be identified by the field technician or analyst actually doing the work.

- Long-term - to eliminate causes of nonconformance. The need for such actions will probably be identified by audits. Examples of this type of action include:

  - Staff training in technical skills or in implementing the QA Program;
  - Rescheduling of laboratory and/or sampling routines to ensure analysis within allowed holding times;
  - Identifying vendors to supply reagents of sufficient purity for field work;
  - Revising Contractor QA system or replacing personnel;
  - Personnel reassignment; and
  - Field instrumentation replacement.

For either immediate or long-term corrective actions, the steps comprising a closed-loop corrective action system are as follows:

- Define the problem;
- Assign responsibility for investigating the problem;
- Investigate and determine the cause of the problem;
- Determine a corrective action to eliminate the problem;
- Assign and accept responsibility for implementing the corrective action;
- Establish effectiveness of the corrective action and implement the correction; and
- Verify that the corrective action has eliminated the problem.

Depending on the nature of the problem, the corrective action employed may be formal or informal. In either case, occurrence of the problem, corrective action employed, and verification that the problem has been eliminated will be documented.

In addition, if the corrective action results in the preparation of a new standard or calibration solution(s), then a comparison of the new versus the old solution will be performed and the results supplied with the weekly QC submittal as verification that the problem has been eliminated.

13.1 Field Situations

Deviations from quality in field operations that require corrective action in the field will be identified by field audits as described in Section 10.0 and by other more immediate occurrences, such as equipment malfunction and on-site observations by the field supervisor. Once the problem has been identified, prompt and appropriate action will be taken by the field staff Task Manager or field supervisor to correct the situation. After a corrective action has been implemented, its effectiveness will be verified and documented in the site log. If the action does not resolve the problem, appropriate personnel will be assigned by the Program Manager or Task Manager to investigate and effectively remediate the problem.

Documentation of all corrective action is required. Immediate corrective actions taken in the field will be documented in the field logbooks and approved by the field supervisor or Task Manager. Corrective actions which result in deviations from the Work Plan or QAPjP will also be documented in a memorandum to the Arthur D. Little Project Manager and QA Officer. They will ensure appropriate changes are incorporated into the final report. Corrective actions initiated as a result of a field audit must be documented in a memorandum from the Task Manager to the Program QA Officer.

13.2 Laboratory Situations

If weaknesses or problems are uncovered during system or performance audits or QC sample analysis, corrective action will be initiated immediately. The DataChem Laboratories Project Manager, Analytical Coordinator, QA Coordinator, and analyst must be involved in the corrective action. If previously reported data or project schedule or budget will be affected, then the corrective actions planned will be directly reported to the DataChem Laboratories Project Manager, Arthur D. Little Program Manager, Arthur D. Little Task Manager, and Arthur D. Little Lead Chemist. Corrective actions may also be initiated by the analyst as required from daily review of control charts.

Corrective action might include, but not necessarily be limited to: recalibration of instruments using freshly prepared calibration standards; replacement of lots of solvent or other reagents that give unacceptable values; instrument repair, additional training of laboratory personnel in correct implementation of sample preparation and analysis methods; and reassignment of personnel, if necessary, to improve the overlap between operator skills and method requirements.

14.0 Quality Assurance Reports to Management

14.1 Laboratory Reports

Each daily report generated has a QA section associated with the text. Any matrix characteristics or other physical parameters are noted. The laboratory must confirm that all characteristics indicated by field investigation team match the sample being analyzed by the laboratory. Any discrepancies cause the analysis sequence to be halted.

Normal submissions to the USAEC Chemistry Branch include the IRDMIS submissions (Section 8.0) and the results of QC activities. During those periods when analyses are being conducted, all QC charts (tabular and graphical), as described in Section 12.0, must be submitted to the USAEC Chemistry Branch and Arthur D. Little on a weekly basis. The QC report must be provided to the Chemistry Branch and Arthur D. Little no later than five working days after analyses for a week are completed. Analysis data shall be defined by the day the analytical instrument was run. All points which indicate an out-of-control situation must be evaluated and explained. Any corrective measures and reanalysis of samples must be fully explained and documented, including procedural changes to prevent recurrence. Printouts generated from control chart software programs provided by USAEC shall be utilized, when available. A checklist included with each control chart submission is shown in Appendix Q of the *USATHAMA Quality Assurance Program*, January 1990.

As an appendix to the project final report, the QAC, in coordination with the Analytical Task Manager and the Project Manager, will provide tabulation of all QC sample data, as well as specific observations delineating the control effectiveness for each analytical method. These observations will include the following:

- QC samples in each lot and how analytical results were combined to prepare control charts;
- Spike levels and rationale for choosing those levels;
- Possible effects on environmental sample results of detected concentrations in method blanks; and
- Unique matrix characteristics of environmental samples.

If any time during the analytical effort a process was not in control, a discussion will be submitted on:

- Rationale for judging a point as in control, if it appears to satisfy an out-of-control criterion listed in Section 12;
- Investigation of the out-of-control situation;
- Actions taken to bring the process back into control;
- Actions taken to ensure that the out-of-control situation did not recur; and
- Disposition of data acquired while the process was out-of-control.

14.2 Program QA Officer and Lead Chemist Reports

The Arthur D. Little Program QA Officer and the Lead Chemist will routinely generate reports to maintain the Program and Task managers informed of the QA/QC activities during the course of the Fort Devens project. These reports will be in the form of a memorandum and will address any findings encountered during their audits and reviews.

Appendix A: DataChem Laboratories Quality Assurance Program Plan

QUALITY ASSURANCE PROGRAM PLAN

for

U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY

September 1991

Laboratory Analysis of Environmental Samples

DCL Document QA-3/87

DataChem Laboratories
960 West LeVoy Drive
Salt Lake City, Utah 84123

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1.0
DOCUMENT IDENTIFICATION

Document Title:	Quality Assurance Program Plan for USATHAMA
Document Control Number:	QA-3/87
Organization:	DataChem Laboratories (DCL) 960 W. LeVoy Dr. Salt Lake City, Utah 84123
Director:	James H. Nelson, Ph.D. Phone: 801-266-7700
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2.0
INTRODUCTION

This document is the DCL Quality Assurance/Quality Control Plan, prepared in compliance with the requirements of the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) with analytical laboratory services in support of the implementation of various installation restoration programs. This plan adheres to, and is an implementation of, the USATHAMA QA Program, January 1990, First Edition.

DCL is committed, in strictly following this plan, to provide to USATHAMA analytical data that are of a quality that may be used in litigation. All deviations from this plan or the USATHAMA QA Program will be submitted to USATHAMA for approval prior to implementation in the laboratory. Such deviations will be properly and fully documented.

DCL has conducted analyses for USATHAMA since 1984 under the 1982 USATHAMA QA Program, the Second Edition (March 1987) of the 1985 USATHAMA QA Program, and the January 1990 USATHAMA QA Program, First Edition.

3.0
ORGANIZATION AND RESPONSIBILITIES

3.1 Introduction

Ultimate responsibility for the conduct of all projects, and approval for the implementation of all programs at DCL resides with the Laboratory Director, Dr. James H. Nelson. Functional responsibility for the analytical work is delegated to the Project Manager, Mr. David W. Gayer; to the Analytical Task Managers, Mr. A. Brent Torgensen, and Mr. Richard Wade; and to the Quality Assurance Coordinator, Mr. Ronald H. Marsden.

3.2 Laboratory Director

The Laboratory Director is responsible to assure that DCL resources are adequately allocated to the project and that sufficient staffing and equipment are provided. He oversees and supports the Quality Assurance Coordinator.

3.3 Project Manager

The Project Manager has the responsibility of communication with the USATHAMA Program Contract Officer and oversees and supports the Analytical Task Managers in development, implementation, and operation of the analytical program organization. He is directly responsible for the interpretation of the provisions of the contract for DCL. The Project Manager is also responsible to assure that QA/QC recommendations and corrective actions are implemented.

The Project Manager is authorized to conduct official discussions with the Program Contract Officer concerning the original contractual agreement and delivery orders, and any subsequent modifications to the contractual agreement and/or delivery orders. Laboratory personnel matters are decided in concert with the Analytical Task Manager and appropriate Section Managers.

3.4 Analytical Task Manager

The Analytical Task Manager has the responsibility of implementing the USATHAMA 1990 QA Plan, and for coordinating the sample analysis flow in the laboratory. This will be achieved through the following:

1. Assuring the provision of sufficient equipment, laboratory space, resources, personnel, and quality reagents and materials to properly conduct the required analyses;

2. Supporting the Quality Assurance Coordinator;

3. Submitting documented analytical methods and laboratory certification data to the USATHAMA Project Officer prior to the analysis of field samples;

4. Ensuring that all provisions of the approved Project Quality Control Plan are fully implemented in the laboratory;

5. Ensuring the implementation of corrective action for any QA/QC deficiencies.

The Analytical Task Manager has the authority to suspend analytical work for quality control problems and to implement corrective actions recommended by the Quality Assurance Coordinator. He also has authority to accept or reject increases in the delivery rate of samples, within the bounds set by the contract. He confers with section managers and the Project Manager on personnel matters when they impact on the project.

3.5 Quality Assurance Coordinator

The Quality Assurance Coordinator (QAC) has the responsibility of establishing, overseeing, and auditing specific procedures for documenting, controlling, and validating analytical data quality. This is accomplished, in part, through the following:

1. Monitoring the QA and QC activities of the laboratory to ensure conformance with authorized policies, procedures, and good laboratory practices, and recommending improvements as necessary;

2. Informing the Project Manager and/or the Analytical Task Manager of noncompliance with the approved QA Program;

3. Requesting standard analytical reference materials from USATHAMA;

4. Ensuring that all records, logs, standard operating procedures, project plans and analytical results are maintained in a retrievable fashion;

5. Ensuring that standard operating procedures and project QA/QC plans are distributed to all appropriate laboratory personnel;

6. In consultation with the analysts and the Analytical Task Manager, establishing appropriate analytical lot size, including the correct QC samples;

7. Establishing the correct procedures and criteria for evaluating whether analytical performance is acceptable and in-control;

8. Ensuring that samples are received and logged properly, including lot sizing, introduction of required QC samples, and numbering of field samples and control samples;

9. Reviewing all laboratory data before those data are released, verifying that data were collected properly under an in-control analytical system;

10. Ensuring that the DCL quality control chemist, or appropriate analysts, are properly preparing QC samples;

11. Maintaining quality control charts, ensuring timely distribution of such charts, documenting corrective actions, and ensuring that analysts implement and document corrective actions as they become necessary;

12. Ensuring that sample logs, instrumentation logs, and all QC documents are properly maintained, including frequency of entries;

13. Discussing control chart results with the Analytical Task Manager and submitting updated, current charts to the USATHAMA Project Officer on a weekly basis, or as required by USATHAMA;

14. Maintaining an awareness of the entire laboratory operation to detect conditions which might jeopardize controls of the various analytical systems;

15. As directed by USATHAMA, auditing sampling documentation and procedures to ensure proper labeling, handling, transportation, and storage.

The Quality Assurance Coordinator has the authority to:

1. Approve all analytical reports;

2. Reject analytical data which does not meet applicable quality control criteria;

3. Require re-performance of sample analyses which are determined to be out-of-control;

4. Evaluate data and determine apparent long-term trends which may require corrective action;

5. Suspend analytical work, when necessary, to assure corrective actions are taken and that an analysis is again in control.

The Quality Assurance Coordinator also attends and participates in conferences for discussion of quality control and quality assurance problems and procedures.

4.0
CERTIFICATION

4.1 Laboratory Certification

DCL, as a laboratory, rather than as individual analysts, certifies as proficient in conducting analyses for USATHAMA. Each member of the organization has the education and training necessary to enable that individual to perform assigned functions. A personnel training file is maintained for each individual. Each individual updates the training file as necessary.

Management personnel have earned a Baccalaureate degree from an accredited college or university.

Analytical Chemists have earned a Baccalaureate Degree in Science or related fields from an accredited college or university.

Technical Staff have applicable training, including on the job training, and/or experience in related fields.

4.2 Analytical Methods

Analytical methods used for the analysis of environmental samples are described in a set of written instructions completely defining the procedure to be followed to process a sample and obtain an analytical result. An analytical method describes, as a minimum, the analytes for which it is valid, the matrix type, sample preparation, reagent and standards preparation, instrument calibration, and computations used to evaluate the analytical results. Standards and quality control sample requirements are also defined.

Analytical methods are either supplied by USATHAMA or, with approval, developed by DCL. The documentation for proposed methods development includes:

1. The submission of documentation to USATHAMA.
2. A statement of the problem.
3. A description of the technical approach to include specific details on procedures, solvents, instrumentation, etc.
4. An estimate of resources required (to include labor hours, funds and schedule).

When the testing of the analytical procedures has been successfully completed, the method is documented in the standardized USATHAMA format. The format for documentation of all analytical methods is provided in Table 1. The format for data analysis is established by USATHAMA-provided statistical analysis computer software. Updates to the software are implemented upon receipt.

Table 1.
FORMAT FOR DOCUMENTATION OF METHOD CERTIFICATION

I. **Summary**
   A. Analytes
   B. Matrix
   C. General Method

II. **Application**
   A. Tested Concentration Range
   B. Sensitivity
   C. Reporting Limit
   D. Interferences
   E. Analysis Rate
   F. Safety Information

III. **Glassware and Chemicals**
   A. Glassware/Hardware
   B. Instrumentation
   C. Analytes
   D. Reagents and SARMs

IV. **Calibration**
   A. Initial Calibration
   B. Daily Calibration

V. **Certification Testing**

VI. **Sample Handling and Storage**
   A. Sampling Procedure
   B. Containers
   C. Storage Conditions
   D. Holding Time Limits
   E. Solution Verification

VII. **Procedure**
   A. Separations
   B. Chemical Reactions
   C. Instrumental Analysis
   D. Confirmational Analysis

VIII. **Calculations**

IX. **Daily Quality Control**
   A. Control Samples
   B. Control Charts

X. **References**

XI. **Data**

The analytical method, once certified, is followed for all USATHAMA analyses. Instrumental conditions are optimized within the limits specified by method and documented by the analyst. Any deviation, other than the optimization of instrumental conditions, is pre-approved by USATHAMA before implementation.

All copies of USATHAMA-certified methods are individually numbered. Each distributed method copy must be signed for and dated. A comprehensive list of all distributed methods is kept by the Quality Assurance Coordinator.

4.3 Method Certification

Before field samples may by analyzed by the laboratory, the methods of analysis must be certified. Certification for selected methods, accomplished under other USATHAMA contracts, may be determined by USATHAMA to be acceptable for the work performed under this contract for identical analytes and matrices. If analytes are required for a particular certified method in addition to those which have already been certified, the additional analytes are appended to the current certified method by following full certification procedures for the additional analytes. The current certified method standards, concentrations and analytical conditions are used to certify the additional compounds.

Some methods, including calibration of test and measurement equipment, do not require certification, due to either the nature of the measurement or the intended use of the data. When such methods are part of a project, USATHAMA will not provide a standardized method. However, laboratories must submit sufficient information in test plans, work plans, and project QC plans to describe exactly the procedures to be used. A copy of a proposed method must be submitted to the USATHAMA Chemistry Branch before it is used on any project.

The following methods do not require USATHAMA certification by the USATHAMA Chemistry Branch: temperature, conductivity, pH, oil and grease, hardness, asbestos, alkalinity (carbonate/bicarbonate/hydroxide), total organic carbon, biochemical oxygen demand, chemical oxygen demand, total dissolved solids, total suspended solids, totals solids, total petroleum hydrocarbons, salinity, and acidity.

4.3.1 Written Method

A draft of the analytical method proposed for certification is submitted to USATHAMA for approval with the precertification performance data package.

4.3.2 Standards

Standard Analytical Reference Materials (SARMs), provided by USATHAMA, are used in all method certification analyses. DCL obtains suitable, certified Reference Materials from the EPA or other commercial sources for analytes for which USATHAMA is not able to provide SARMs. Standard water and standard soil are used by DCL for all USATHAMA analyses done.

4.3.3 Standard Water

Standard water samples are prepared by adding a known quantity of target analyte to a known volume of water. The volume of water is specific in the method being performed. All target analytes for the method are added. ASTM Type I grade water is used for inorganic methods. ASTM Type II grade water containing 100 mg/L each of added sulfate and chloride is used for organic methods. The method and reagents used to prepare spiking solutions are specified in the standardized methods.

4.3.4 Standard Soil

Standard soil samples are prepared by adding a known quantity of target analyte to a known weight of selectively blended standard soil as provided by the Chemistry Branch of USATHAMA.

4.3.5 Precertification Calibration

Before initiating method certification, precertification calibration is performed. DCL holds discussions with USATHAMA delineating anticipated environmental concentrations. The concentration range tested includes the Target Reporting Limit (TRL). Additional concentrations of calibration standards may be included for expanding the range of certification. Duplicate analyses are performed on all of the calibration standards.

The certified check standards are obtained from a source other than USATHAMA, whenever possible. In the absence of suitable commercially prepared mixtures, the DCL Quality Control Chemist prepares appropriate mixtures from certified pure stock reagents. The mixtures contain the analyte(s) of interest at concentrations near the high end of the certification range.

The calibration standard data is tabulated and graphed for analysis of Lack of Fit (LOF) and Zero Intercept (ZI), then submitted to USATHAMA for evaluation. The check standard results are required to fall within the acceptability limits defined by the originator.

4.3.6 Certification

Certified methods meet the following conditions: The Target Reporting Limit (TRL) and the range of certification are selected in consultation with USATHAMA. A pre- certification analysis is performed and reported to USATHAMA, with a copy of the analytical method. Upon approval from USATHAMA, a Class 1, Class 1A, Class 1B, or Class 2 certification process is initiated. See Table 2.

Data derived from certification is processed using USATHAMA supplied software, and submitted to USATHAMA for evaluation. The method Certified Reporting Limit (CRL) and certified range are determined from this data evaluation.

Methods certified under previous editions of the USATHAMA Quality Assurance Program and determined by USATHAMA to be valid for current work do not require recertification.

All certification data are properly maintained in archive files.

4.3.7 Method Modifications and Control

Any modifications, additions, or deletions proposed to any USATHAMA-certified method must be submitted to USATHAMA for approval before such a change is made. Following approval, the revised method (with changes plainly noted) shall be distributed to appropriate laboratory personnel as described in DCL SOP-GLP-002, and the old method collected for retirement.

4.4 Analyst Training

An analyst certifying a new method is qualified to perform that method during routine field sample analysis. An analyst who is required to perform on a procedure which has already been certified is required to satisfactorily analyze an appropriate set of quality control samples to demonstrate ability to perform the method. The demonstration sample data must pass current quality control criteria. Successful certification performance is reflected by an addition to the analyst's training file.

The analyst prepares all data records and a data package, as required for field sample analysis data. The data and the data package must be approved by Quality Assurance. The data and data package are maintained in archives.

Table 2.
NUMBERS AND CONCENTRATIONS OF CALIBRATION STANDARDS (LINEAR AND ZERO-INTERCEPT)

PRECERTIFICATION - CLASS 1

Minimum Testing Range (MTR): 12 Standards + 1 Check Standard (SC)
Blank, *0.5, 1, 2, 5, & *10 TRL (Duplicate) + CS
MTR + 1 Order of Magnitude Extension: 18 Standards + 1 Check Standard (CS)
Blank, *0.5, 1, 2, 5, 10, 20, 50, & *100 TRL (Duplicate) + CS
MTR + 2 Orders of Magnitude Extension: 24 Standards + 1 Check Standard (CS)
Blank, *0.5, 1, 2, 5, 10, 20, 50, 100, 200, 500, & *1000 TRL (Duplicate) + CS

PRECERTIFICATION - CLASS 1A

Minimum Testing Range (MTR): 8 Standards
Blank, *0.5, 2, & *10 TRL (Duplicate)
MTR + 1 Order of Magnitude Extension: 12 Standards
Blank, *0.5, 2, 10, 50, & *200 TRL (Duplicate)
MTR + 2 Orders of Magnitude Extension: 16 Standards
Blank, *0.5, 2, 10, 50, 200, 500, & *2000 TRL (Duplicate)

PRECERTIFICATION - CLASS 1B

Minimum Testing Range (MTR): 8 Standards + 1 Check Standard (CS)
Blank, *0.5, 2, & *10 TRL (Duplicate) + CS
MTR + 1 Order of Magnitude Extension: 12 Standards + 1 Check Standard (CS)
Blank, *0.5, 2, 10, 50, & *200 TRL (Duplicate) + CS
MTR + 2 Orders of Magnitude Extension: 16 Standards + 1 Check Standard (CS)
Blank, *0.5, 2, 10, 50, 200, 500, & *2000 TRL (Duplicate) + CS

PRECERTIFICATION - CLASS 2

(Not Required)

INITIAL CALIBRATION - CLASS 1

Minimum Testing Range (MTR): 7 Standards + 1 Check Standard (CS)
Blank, *0.5, 1, 2, 5, *10, & *10 TRL + CS
MTR + 1 Order of Magnitude Extension: 10 Standards + 1 Check Standard
Blank, *0.5, 1, 2, 5, 10, 20, 50, *100, & *100 TRL + CS
MTR + 2 Orders of Magnitude Extension: 13 Standards + 1 Check Standard
Blank, *0.5, 1, 2, 5, 10, 20, 50, 100, 200, 500, *1000, & *1000 TRL + CS

* 10 percent to 25 percent Range Extension

Table 2
(Continued)

INITIAL CALIBRATION - CLASS 1A

Minimum Testing Range (MTR): 5 Standards
Blank, *0.5, 2, *10, & *10 TRL
MTR + 1 Order of Magnitude Extension: 7 Standards
Blank, *0.5, 2, 10, 50, *200, & *200 TRL
MTR + 2 Orders of Magnitude Extension: 9 Standards
Blank, *0.5, 2, 10, 50, 200, 500, *2000, & *2000 TRL

INITIAL CALIBRATION - CLASS 1B

Minimum Testing Range (MTR): 5 Standards + 1 Check Standard (CS)
Blank, *0.5, 2, *10, & *10 TRL + CS
MTR + 1 Order of Magnitude Extension: 7 Standards + 1 Check Standard
Blank, *0.5, 2, 10, 50, *200, & *200 TRL + CS
MTR + 2 Orders of Magnitude Extension: 9 Standards + 1 Check Standard
Blank, *0.5, 2, 10, 50, 200, 500, *2000, & *2000 TRL + CS

INITIAL CALIBRATION - CLASS 2

Minimum Testing Range (MTR): 6 Standards
Blank and 1 TRL (Triplicate)

DAILY CALIBRATION - CLASS 1/CLASS 1A/ CLASS 1B

Minimum Testing Range (MTR): 2 Standards
*10 & *10 TRL
MTR + 1 Order of Magnitude Extension: 2 Standards
*100 & *100 TRL
MTR + 2 Orders of Magnitude Extension: 2 Standards
*1000 & *1000 TRL

DAILY CALIBRATION - CLASS 2

Minimum Testing Range (MTR): 4 Standards
Blank and 1 TRL (Duplicate)

Table 2
(Continued)

CERTIFICATION - CLASS 1

Minimum Testing Range (MTR): 9 Initial, 6 Daily
MTR + 1 Order of Magnitude Extension: 12 Initial, 6 Daily
MTR + 2 Orders of Magnitude Extension: 15 Initial, 6 Daily

CERTIFICATION - CLASS 1A

Minimum Testing Range (MTR): 5 Initial
MTR + 1 Order of Magnitude Extension: 7 Initial
MTR + 2 Orders of Magnitude Extension: 9 Initial

CERTIFICATION - CLASS 1B

Minimum Testing Range (MTR): 6 Initial, 6 Daily
MTR + 1 Order of Magnitude Extension: 8 Initial, 6 Daily
MTR + 2 Orders of Magnitude Extension: 10 Initial, 6 Daily

CERTIFICATION - CLASS 2

Minimum Testing Range (MTR): 6 Initial

INITIAL FIELD SAMPLE LOT - CLASS 1

Minimum Testing Range (MTR): 9 Initial
MTR + 1 Order of Magnitude Extension: 12 Initial
MTR + 2 Orders of Magnitude Extension: 15 Initial

INITIAL FIELD SAMPLE LOT - CLASS 1A

Minimum Testing Range (MTR): 5 Initial
MTR + 1 Order of Magnitude Extension: 7 Initial
MTR + 2 Orders of Magnitude Extension: 9 Initial

Table 2
(Continued)

INITIAL FIELD SAMPLE LOT - CLASS 1B

Minimum Testing Range (MTR): 6 Initial
MTR + 1 Order of Magnitude Extension: 8 Initial
MTR + 2 Orders of Magnitude Extension: 10 Initial

INITIAL FIELD SAMPLE LOT - CLASS 2

Minimum Testing Range (MTR): 6 Initial

ADDITIONAL FIELD SAMPLE LOT - CLASS 1/CLASS 1A/CLASS 1B

Minimum Testing Range (MTR): 2 Daily
MTR + 1 Order of Magnitude Extension: 2 Daily
MTR + 2 Orders of Magnitude Extension: 2 Daily

ADDITIONAL FIELD SAMPLE LOT - CLASS 2

Minimum Testing Range (MTR): 4 Daily

5.0
SAMPLE HANDLING AND ANALYSIS

5.1 Sample Management

In most instances, DCL does not perform sample collection, but receives samples from designated field crews. Samples received by DCL are received by designated sample custodians. The protocols of sample management are delineated below.

5.1.1 Sample Containers

As directed by USATHAMA, DCL will supply sample bottles and/or shipping coolers for use in the collection of field samples. A copy of DCL's "Field Sampling Information," to be used as guidance in sampling and in the completion of chains-of-custody, is included in the initial shipment of coolers to the field sampling site. All sample containers shall be cleaned before use according to the protocols specified in Appendix C. Use of commercially cleaned bottles is acceptable provided that cleaning is performed as specified in Appendix C or meets the requirements of the EPA's Contract Laboratory Program.

Generally, for water samples, this includes: septum-sealed glass vials for volatile compounds; amber glass bottles with Teflon-lined lids for organic constituents other than volatiles; and polyethylene bottles for inorganic analytes. Exceptions are noted in the certified method. For soil and sediment samples wide-mouth amber-glass bottles shall be used. Preservatives, as delineated in the DCL USATHAMA Analyte Summary (Appendix B), are provided (as necessary) with sample containers shipped to the field, for proper addition at the site.

5.1.2 Sample Receipt

Samples are received at DCL by the designated Sample Receipt Officer (SRO), or his designee. At the time of receipt of a sample shipment, the sample shipping containers are opened and the samples are inspected. A Sample Receipt Form is initiated at this time. This form includes entries for date and time of receipt, airbill number, a record of the condition of seals on the shipping container and samples, documentation present, temperature and general condition of the shipment, and correlation of sample document and sample labeling information.

Any discrepancies between the samples and the documentation, including missing, broken, or damaged samples, will be reported to USATHAMA or its contractor within 24 hours.

The SRO or his designee signs the field chain-of-custody record at the time that the shipping container is opened. In the case of water samples, which do not usually require splitting, the SRO or his designee opens the shipping container and completes the sample inspection form and field chain-of-custody record. Sufficient copies of the field chain-of-custody record are made to allot one copy for each analytical procedure, plus one for moisture and one as a back-up.

5.1.3 Sample Logging

The field chain-of-custody record is used by the Sample Receipt Coordinator (SRC) to initiate sample logging procedures. Initial logging entries include field sample number, date of receipt at DCL, analyses requested, and comments on sample condition at the time of receipt as noted on the Sample Receipt Record. These are recorded in both a computer based log and in a bound logbook. After sample lotting is completed, the USATHAMA sample identification number for each sample and analysis is entered into the logs.

5.1.4 Sample Splitting

Following initial sample inspection, the SRC splits the samples into the required number of aliquots (one for each analytical procedure, one for moisture if the sample is a soil, and a large portion for back-up). The SRO properly labels the aliquots with the field sample identification number and the method of analysis, and relinquishes custody of the sample aliquots to the SRC.

5.1.5 Sample Lotting and Labeling

The number of samples which can be analyzed by a given method on a single day, as determined by the rate-limiting step in the analytical scheme, is designated as a "lot". The samples in a lot are labeled with a USATHAMA sample identification number consisting of a three letter lot code and individual three number sample designations (e.g. AAA001, AAA002). As split sample aliquots for a particular analytical procedure are received by the SRC, they are given the next alphabetical lot designation in sequence. Samples received and split at various times are grouped together in the same lot such that sample holding times are not jeopardized. The unique sample number is written in black permanent marker on white laboratory labeling tape, which is prominently placed on each sample container.

Quality control (QC) samples are a part of every lot, and are spiked according to the specific method requirements. The QC samples are provided upon request of the analyst.

5.1.6 Sample Storage

Samples are stored in a location appropriate to the holding requirements of the requested analytes. Heat-sensitive, light-sensitive, radioactive, or other samples having unusual physical characteristics or requiring special handling, are properly stored and maintained.

5.2 Chain-of-Custody

DCL maintains chain-of-custody records for all USATHAMA samples received at the laboratory.

A copy of applicable field chain-of-custody records is maintained with each sample lot. In addition, each lot of samples is maintained under a separate laboratory chain-of-custody record. The chain-of-custody includes unique sample number(s), date and time, source of sample(s), analyses required, signatures of relinquishing and receiving entities, and any other pertinent information. Copies of DCL's field and in-house chains-of-custodies for USATHAMA projects are provided in Appendix D.

5.3 Sample Handling Procedures

After samples have been received, split, and lotted, those not requiring extraction procedures are transferred to a central walk-in cold storage area. They are stored in this area until they are scheduled for analysis. Samples not requiring extraction procedures are prepared for analysis, within the required holding times, by the analyst or by a technician working under the direction of the analyst. These samples are usually analyzed within hours after preparation.

Samples which require extraction, distillation, or digestion procedures are prepared for analysis by the appropriate Inorganic or Organic Sample Preparation groups after lotting procedures have been completed. Extracts or distillates are stored in refrigerators in appropriate analytical areas of the laboratory.

The samples and extracts are maintained in their designated lots and under chain-of-custody, at all times. Separate preparation logbooks are maintained by the sample preparation groups to document sample handling.

5.4 Toxicity Characteristic Leaching Procedure

Samples which require Toxicity Characteristic Leaching Procedure (TCLP) are split and assigned a unique three-letter lot code. Chains-of-custody for these samples are signed off in the same manner as other samples requiring a USATHAMA-certified analysis. At the same time, chains-of-custody are printed (but not "initiated") for all prospective analyses to be generated from the TCLP leachate(s).

Once the original sample has been satisfactorily leached, both the chain-of-custody and any remaining original sample are transferred to Long Term Storage. The chains-of-custody for all generated leachates are now initiated by TCLP personnel. These leachates (along with their chains-of-custody) are stored and handled as any other USATHAMA samples which have been prepared for analysis.

The chains-of-custody for the original sample and the leachates are cross-referenced to facilitate traceability.

5.5 Holding Times

The holding times specified in DCL's USATHAMA Analyte Summary (Appendix B) are adhered to for all USATHAMA samples, extracts, distillates, and digestates.

5.6 Sample Analysis

5.6.1 Standards

Analytical standards are prepared either from Standard Analytical Reference Materials (SARMs) or Interim Reference Materials (IRM) supplied by USATHAMA, or from standard materials obtained by DCL from the EPA, the National Institute of Standards and Technology (NIST), or other commercial sources. Secondary standard materials may be used when SARM materials are available in only limited quantity. The secondary standards, which must be positively identified with an estimation of purity, are referenced to SARMs and periodically checked against them.

Standard materials procured from commercial sources other than USATHAMA, the Environmental Protection Agency (EPA), or the NIST are considered as "off-the-shelf" materials. The purity and identity of these materials is established from both analysis documentation supplied by the vendor and DCL analytical data. Materials are characterized by two independent methods whenever possible, including, but not limited to IR, GC, GC/MS, HPLC, and other inorganic techniques.

Metals are traceable to NIST, whenever possible. "Off-the-shelf" materials are characterized against EPA or NBS known standards whenever possible. All SARMS are stored in the quality control laboratory, under controlled access conditions. Generally, organic compounds are stored under refrigeration, while metals solutions are stored at room temperature.

5.6.2 Solutions

Analytical standard working solutions are normally prepared by the analyst performing the analysis, in accordance with the protocol defined in the approved analytical method. In some analytical procedures, a designated analyst prepares the standards, while other analysts carry out the procedure.

As new or replacement standard solutions are prepared, they are validated against either the previously used standard, a commercially prepared quantitative standard, or a standard prepared by another analyst for the purpose of validation.

Although validation acceptance criteria are established for each analytical method, protocol guidelines for acceptance of a new solution is that it is found, by analysis, to be within ±5% of the target value. All validations are documented either in the analyst's notebook or in a standards preparation logbook unique to USATHAMA and the analytical area using the standards.

5.6.3 Sample Preparation

Soil and water field samples are prepared for analysis according to the protocol defined in the analytical method for the specific analyte(s) being analyzed. Procedures for the preparation of mixed-matrix field samples, such as sediment, sludge, sewer, or lake-bottom samples, are discussed with USATHAMA on a case-by-case basis.

5.6.4 Instrument Calibration

The USATHAMA QA Program delineates, in detail, the requirements for instrument calibration for precertification, full method certification, initial calibration for analysis work, and daily calibration during sample analysis. DCL has implemented these guidelines for all USATHAMA work, as follows. Also see Section 4.3.6 (Certification) for additional details.

Instruments are tuned, as applicable, and the required number and concentrations of standards are analyzed daily with each lot of samples. Calibration criteria are either passed or corrective action is pursued by the analyst. If daily calibration criteria are not met, then initial calibration procedures are instituted to bring the analytical system back into calibration.

5.6.5 Initial Calibration

During initial calibration, a minimum of one blank and five calibration standards (Class 1) or one blank and three calibration standards (Class 1A and Class 1B) that bracket the certification testing range is analyzed singularly on one day. The concentrations of the calibration standards, in the solvent that results from all the preparation steps of the method, take into account any concentration steps that are part of the method. Concentrations in the solvent correspond to those in an environmental matrix as if the method preparation steps had been performed.

In addition to the initial calibration standards, Class 1 and 1B methods require the analysis of calibration check standards (Section 5.6.7). During a Class 1 or Class 1B initial calibration, a calibration check standard is analyzed at the completion of calibration. If the method requires what could be an initial calibration each day analysis is performed, then the calibration check standards are analyzed once a week rather than each day.

If the results of the calibration check standard are not acceptable, immediate reanalysis of the calibration check standard is required. If the results of the reanalysis still exceed the limits of acceptability, the system is considered to have failed calibration. Sample analysis is halted and will not resume until successful completion of initial calibration. Corrective actions taken to restore initial calibration are documented in the analysts' notebook.

5.6.6 Daily Calibration

Calibration standards are analyzed each day to verify that instrument response has not changed from previous calibration. Each day before sample analysis, the highest concentration standard is analyzed. The response must fall within the required percentage or two standard deviations of the mean response for the same concentration, as determined from precertification, certification, and prior initial/daily calibrations. If the response fails this test, the daily standard is reanalyzed. If the response from the second analysis fails this range, initial calibration is performed before analyzing samples.

Each day after sample analyses are completed, the highest concentration standard is analyzed. If the response is not within the required percentage or two standard deviations of the mean response from precertification, certification, and prior initial/daily calibrations, the daily standard shall be reanalyzed. If the response from the second analysis fails the range, the system is considered to have failed calibration. Initial calibration is performed and all samples analyzed since the last acceptable calibration are reanalyzed.

For non-linear or non-zero-intercept calibration curves, daily calibration consists of analysis of the low, middle, and high standards at the beginning of the day. When sample analyses are completed at the end of the day, the low and high standards are analyzed. Instrument responses for each concentration determination must fall within two standard deviations of the mean response, as described previously, for the appropriate standard. For calibrations fitted by the quadratic equation, a minimum of four standards over the certified range are required and the highest level standard analyzed at the end of the day. For all other equations, one more standard than needed to meet the degrees of freedom for any lack-of-fit is required, as a minimum.

5.6.7 Calibration Check Standards

Calibration check standards are required for all Class 1 and 1B methods and are analyzed during precertification and with each initial certification. The calibration check standard contains all analytes of interest for the method in question at a concentration near the upper end of the calibration range. Results of the calibration check standards shall fall within the limits of acceptability as described below:

CASE 1.
A certified check standard is available from the EPA or some other source with both the true value and limits of acceptability specified by the supplier. The results must fall within the limits specified by the supplier, or +/-10 percent for inorganics, +/-25 percent for organics, whichever is less.

CASE 2.
A certified check standard is available from the EPA or some other source with a true value specified but without limits of acceptability. The results must fall within +/-10 percent for inorganics and within +/-25 percent for organics.

CASE 3.
If no certified check standard is available, the contractor laboratory shall prepare a check standard using a second source of reference material. This standard shall be prepared by a different analyst than the one who prepared the calibration standard. If weighing of the material is required, a different balance should be used, if possible. The results must fall within +/-10 percent for inorganics and within +/-25 percent for organics.

CASE 4.
If there is only one source of reference material available, then the calibration and calibration check standards must be prepared from the same material. The standards shall be prepared by different analysts. If weighing is required, different balances should be used, if possible. The results must fall within +/-10 percent for inorganics and within +/-25 percent for organics.

For all cases listed above, after the seventh acceptable calibration check standard, the limits of acceptability are +/- two standard deviations, as determined from the first seven points.

For multi-analyte methods, the calibration check standard contains all analytes of interest. For the check standard to be deemed acceptable at least 2/3 of the analytes must meet the limits of acceptability as defined above (also see Table 3). In addition, if a single analyte falls outside the limits of acceptability for two consecutive times, then the calibration check standard is deemed unacceptable. If a calibration check standard is not acceptable, the procedures detailed above are followed.

Table 3.
MINIMUM NUMBER OF IN-CONTROL POINTS FOR MULTI-ANALYTE METHODS

Required Control Analytes Per Method	Required Number of Data Values Falling Between the UCL and LCL
1	1
2	2
3	2
4	3
5	4
6	4
7	5
8	6
9	6
10	7
11	8
12	8
13	9
14	10
15	10
16	11
17	12
18	12
19	13
20	14
21	14
22	15
23	16
24	16
25	17

5.6.8 Analytical Procedures

All field samples are analyzed according to approved, laboratory certified USATHAMA analytical methods. All deviations shall be approved by USATHAMA prior to implementation. These deviations are also documented in the analyst's notebook.

5.6.9 Second-Column Confirmation

In several GC and HPLC methods (e.g., organochlorine pesticides and explosives), the presence of compounds is routinely confirmed on a second column. The confirmation is usually performed on the basis of a Class 2 certification. Confirmation does not necessarily have to be performed within holding times, but must be accomplished within ten (10) days of sample analysis.

5.7 Data Handling

Although the primary emphasis of the USATHAMA QA Program is the control of sample analysis and the handling of data, record keeping maintains its importance in the overall assessment of the production of quality of data and is used in part to document the control of sample analysis. The degree of rigor used in documenting sampling and analysis activities cannot be understated. All activities require extensive documentation and special handling protocols. All activities are to be performed under chain-of-custody procedures. Particularly in these situations, the attitude is: "If you didn't write it down, you didn't do it."

For most USATHAMA projects, this degree of documentation is required. For some projects, documentation in the form of an EPA CLP package is required. In any case, the records described in this Quality Assurance document shall be maintained and will be available for inspection by USATHAMA.

5.7.1 Data Reduction

Generally, data have been collected during the analysis of samples either into computer based data files or onto hard copy sheets, which, in turn, are either machine generated or hand written. All of the data are eventually compiled in computer files. The data pertaining to analytical standards are either compared to the most recent initial calibration curve, in the case of a daily calibration, or used to generate new initial calibration curves, in accordance with those generated during pre-certification. The appropriate standard curve is used to evaluate the field sample data to determine the amount of analyte present. Finally, all of the computer generated calculations are generated as hard copy output.

5.7.2 Data Validation

Initial data validation is accomplished during data collection through the use of quality control samples and calibration check standards. Errors detected through a review of these monitors by Quality Assurance during analysis are corrected during the data collection phase of the analysis. Only analytically valid data are processed further.

Following an analyst's computer-based reduction of data and production of a numerical results report, the entire assemblage of data is given to a peer analyst for review and validation. The peer analyst checks that the analytical method was followed, that there are no errors in the transcription of data, that the best-fit curve was used, and that the numerical report of data contains no calculation or transcription errors.

The data package is then reviewed by the appropriate Group Leader or Section Manager. The data report is particularly scrutinized to assure that all reported data values are in the proper range or have dilution factors, that the method has been carefully followed, that instrumentation was properly tuned or calibrated, and that the instrumental data was properly interpreted. A general review of the data package is also made to assure that all required documentation is present.

The final step in data validation is the review by Quality Assurance. The content of each data package is closely checked for errors or omissions that would negatively impact on the admissibility of the data in litigation proceedings. Corrective action is initiated and documented as outlined in section 10.0.

5.7.3 Data Reporting

The results for samples analyzed for USATHAMA projects are entered into the USATHAMA-provided software program (IRDMS). Data created using the IRDMS can then be electronically transmitted to USATHAMA Via Potomac Research Inc. (PRI), or a diskette together with hard copy printouts can be submitted.

Data is entered on a coding form by the analyst, which is verified by the peer checker and, group leader/section manager. QA personnel review data for obvious errors. These data are encoded onto a diskette, checked through two USATHAMA software routines, then printed out and verified by visual inspection by a Data Entry Specialist. Verified analytical results are then submitted to USATHAMA. DCL retains a copy diskette of all data submitted.

All information pertaining to the analysis of a lot of samples is collected into a data package at the completion of analysis. The contents of data packages varies with methods of analysis. The package is reviewed by Quality Assurance to eliminate technical errors that might affect the litigation quality of the data. The reported data is also reviewed by Data Entry for completeness before release.

All data packages are archived at DCL until a task or delivery order at a particular installation is complete. At that time, all pertinent documentation filed in appropriately-labeled boxes is delivered either to USATHAMA directly, or to the prime contractor responsible for final review of the data packages. In the second case, the prime contractor is responsible for the delivery of DCL data boxes to USATHAMA.

6.0
ANALYTICAL SYSTEM CONTROLS

6.1 Sample Control

As discussed in the section of this QA Plan on Sample Management, DCL is not generally responsible for the collection of samples from sites in the field. However, DCL efforts in sample control may extend into field sample collection. As directed by USATHAMA or the prime contractor, DCL provides proper sample collection bottles, sample preservatives, labeling material, sample shipping containers (coolers), and technical assistance to field sample collection crews. DCL also works in concert with USATHAMA or the prime contractor on sample shipping and receiving.

Samples received at DCL are under the control of Sample Receipt personnel from receipt at the lab to acceptance by an analyst for extraction or preparation. Samples are not released for processing until all documentation is completed and the samples are properly lotted and labeled. Holding times are closely monitored by the analysts, Sample Receipt and laboratory management.

DCL Project Managers communicate regularly with USATHAMA and/or other involved prime contractors to alleviate sample shipping, holding time, and analysis difficulties.

6.2 Document Control

Document control is primarily the responsibility of Quality Assurance. Sample documents generated in the field during sample collection and shipping are maintained in QA files. Laboratory chain-of-custody records, sample receipt and tracking records, data reporting forms and analysis data packages, and corrective action records are maintained by Quality Assurance. On a schedule determined by contract requirements, QA also archives or otherwise controls all bound notebooks and logbooks containing data pertinent to USATHAMA work.

6.3 Quality Control Samples

Quality control chemists within the Quality Assurance Section of DCL prepare most of the quality control samples required during sample analysis. These samples are prepared from USATHAMA-supplied SARM and IRM stocks, and other reference materials. Other reference materials include EPA, and NIST standard materials, and "off-the-shelf" materials. "Off-the-shelf" materials are analyzed by DCL, with positive identification and estimate of purity, with EPA standard reference materials, where possible, using at least two different methods.

Quality control stock and dilute working solutions are prepared and maintained separately from those used by analysts as standards. Exceptions to this procedure are made only when primary stock material is in very short supply, or when the primary solution is unstable. In these cases, the same primary solution is used to prepare separate dilute working solutions. Samples are prepared in accordance with parameters defined in each analytical method. These parameters include the control analytes, the concentration levels at which the analytes should be spiked, control sample matrix, spike equilibration time, and procedures for preparation of the sample for analysis.

Quality control samples which are not regularly prepared by the quality control chemists include surrogate spiking solutions and spiked samples required in the GC/MS methods for volatile and semi-volatile organic compounds. These surrogate preparations are handled by the GC/MS Group and the Extraction Group, respectively.

Quality control samples are included in every lot of USATHAMA samples, as required in the USATHAMA QA Program and specified in each certified analytical method. The control samples are processed through the entire analytical method and quantitated on the same calibration curve as the field samples. The results for the quality control samples are evaluated first by the analyst, and then by Quality Assurance, to determine their acceptability.

Calibration check standards are prepared by someone other than the person preparing the standards. Calibration check standards are analyzed at the time of an initial calibration, or once per week when routine initial calibrations replace daily calibrations. The analysis results must meet the criteria established by their originator.

6.4 Control Charts

For Class 1, Class 1A, and Class 1B certified methods, control charts are used to monitor the variations in the precision and accuracy of routine analyses and to detect trends in these variations. The construction of a control chart requires initial data to establish the mean and range of measurements. The QC control charts are constructed from data representing performance of the complete analytical method. Data used in control charts is not adjusted for accuracy. Control charts are not used with Class 2 certified methods.

Control charts include the analyte, method number, DCL laboratory code of UB, spike concentration, and chart title. All data presented on a control chart are also presented in tabular form. The following charts may be selected from the USATHAMA-supplied computer control chart program:

1. Single-Day X-Bar Control Chart (High Spike Conc.)
2. Single-Day Range Control Chart (High Spike Conc.)
3. Three-Day X-Bar Control Chart (Low Spike Conc.)
4. Three-Day Range Control Chart (Low Spike Conc.)

In addition, the following information is also included on each control chart:

- Three-letter lot designation for each point, shown on the x-axis;
- Percent recovery (for X-bar control charts), or range (for R control charts) along the y-axis;
- Upper control limit (UCL);
- Upper warning limit (UWL);
- Mean;
- Lower warning limit (LWL), on X-bar charts; and
- Lower control limit (LCL), on X-bar charts.

For some analytes specified by USATHAMA, warning limits on X-bar charts are deleted and replaced by modified control limits based upon data quality specifications.

6.4.1 Control Chart Plotting: Single-Day

The initial control chart is prepared using the four days of certification data closest to the spiking concentration used during analysis. The average (X-bar), average range (R), and control limits for both are updated after each in-control lot for the first 20 lots. Limits established after lot 20 are used for the next 20 lots. Control charts are updated after each 20 lots thereafter, using the most recent 40 points. In interpreting the control charts developed for the initial lots (1-20), the limits established from the previous lots are used to control the current lot.

When modified limits are established, data for samples are accepted if the control data fall between the modified limits. If modified limits have not been established, data for samples are accepted, based upon the recoveries established during certification and the current performance of the method. In updating the control charts, the new data must be combined with the individual values of previous average percent recoveries and not the mean of all previous data. Only lots evaluated as in-control are applicable to the 20 and 40 lot requirements for establishing and updating control chart limits. Out-of-control or outlier points are plotted; however, such lots are not utilized in lot number requirements or control chart calculations.

All recoveries are plotted, whether or not the lot is in-control. Plotted points represent averaged instrument measurements and not the individual measurement values. Each individual recovery measurement value is tested as an outlier using Dixon's Test at the 98% confidence level. If the datum is not classified as an outlier by the test, the point is included in updating the control chart limits. If the datum is classified as an outlier, it is not used in updating the control chart limits. Range data are not subject to outlier testing.

After the first 20 in-control sample lots, control limits are recalculated using only in-control data points. The control limits are then drawn backward to encompass all previous points. Any points falling outside the control limits (UCL or LCL) are dropped from the calculations (but left on the charts) and the control limits recalculated using only points between those limits. This practice of dropping points and recalculating limits is performed only once, at the initialization of stable limits. Charts are then updated with newly calculated control limits and all points plotted.

6.4.2 Three-Point Moving Average

Analytical data for analytes prepared in the single low concentration QC sample are plotted and evaluated on a three-day-moving-average control chart. Data for the surrogates spiked in a standard matrix and used in GC/MS analyses are also charted on a three-day-moving-average control chart. Plotting criteria for the three-point moving average control charts are similar to those described above (Section 6.4.1) for single-day control charts. Data for analytes prepared in duplicate QC samples at high concentrations are plotted and evaluated on single-day control charts.

Computer generated control charts maintained by Quality Assurance are updated and printed weekly, while analysts plot data points by hand as sample lots are analyzed. This allows for both computer maintenance and evaluation of a large data base with software calculation of control limits, and immediate daily surveillance of analytical trends.

6.5 Out-of-Control Conditions

Results of the analysis of quality control samples are reported to QA within 48 hours of completion through the analyst's submission of a Preliminary QC Report.

The analyst quantifies each analyte in the method blank and spiked QC sample each day of analysis. Processing of additional lots will not occur until the results of the previous lots have been calculated, plotted on control charts as required, and the entire analytical method shown to be in control.

An indication of an out-of-control situation may include: A value outside the control limits or classified as outlier by statistical test; A series of seven successive points on the same side of the mean; A series of five successive points going in the same direction; A cyclical pattern of control values, or; Two consecutive points between the UWL and UCL or the LWL and LCL.

If the points for at least two-thirds of the control analytes for a multi-analyte method are classified as in-control, the method is in control and environmental sample data may be reported. A method may be deemed out-of-control even if greater than or equal to 2/3 of the control analytes meet control criteria. Of the remaining control analytes (less than 1/3 possible out-of-control), if one analyte has two consecutive out-of-control points, as defined above, the method is deemed out-of-control. If data points for fewer than 2/3 of the control analytes are classified as in control, the method is considered to be out-of-control and all work on that method must cease immediately. No data for environmental samples in that lot may be reported.

In all cases, investigation by the analyst and the Quality Assurance Coordinator is required to determine the cause of the condition and to decide on appropriate corrective action. The pertinent details of the situation and the corrective action taken are fully documented in a Corrective Action Report (CAR). (See also section 10.0.) Field sample data effected by the situation are evaluated and reanalyzed as necessary.

When a method is determined to be out of control, the analysis of field samples by that method is suspended. Corrective action must be documented and the method must be demonstrated to be in control before analysis of field samples is reinstated. Analytical control is demonstrated through the acceptable analysis of an appropriate set of QA samples.

7.0
PREVENTATIVE MAINTENANCE

All analytical instrumentation used at DCL is maintained to provide consistent, high-quality performance. Most instruments are maintained by the manufacturer, under contract. Each instrument is labeled with a unique number and instrument information peculiar to USATHAMA requirements. Instrument service records and maintenance calibrations are maintained by the appropriate section and in a logbook unique for each instrument.

The primary objective of the instrument maintenance program is to assure the quality of the analytical data generated by the instrument. While there are analytical systems which require absolute calibration, such as balances, the majority of analytical systems used by DCL for the analysis of USATHAMA samples are calibrated at the time of use by the analyst. This is accomplished through generation of a chemical calibration curve, based upon instrument response verses analyte concentration. This curve is used to evaluate field sample data through instrument responses.

Major instrument systems which are calibrated on an "as used" basis are maintained under either an "on call" or a preventative maintenance contract with the manufacturer. Preventative maintenance is scheduled in each instrument contract. When an instrument cannot perform to specifications and DCL technicians cannot return it to specification, a contracted repair service (usually the manufacturer) is called.

Instrument systems which must maintain an absolute calibration, such as analytical balances, are serviced under contract with the manufacturer, usually on an annual basis. Balances are also checked, on at least a weekly basis, for accuracy by Quality Assurance, using NIST-traceable weights. Temperatures of freezers, refrigerators, and walk-in coolers are recorded every working day by QA. When temperatures are noted outside the acceptable range, appropriate personnel are notified for correction. Ovens are calibrated and their temperatures maintained regularly by the appropriate section personnel.

8.0
RECORDKEEPING

8.1 Laboratory Notebooks

Bound, sequentially-numbered laboratory notebooks with pre-numbered pages are utilized by all analysts for analytical recordkeeping. Notebooks are generally issued to and used by an individual analyst. Any loose sheets of data which must be included in a notebook are securely taped into the notebook and signed and dated across the edges, halfway on the inserted sheet and halfway on the notebook page. Each data page is signed and dated by the analyst entering data on that page, as well as reviewed, signed, and dated by a witness. All entries are required to be in black ink. Corrections are made by a single strikeout, which is dated and initialed.

8.2 Logbooks

8.2.1 General

Individual logbook entries are signed and dated by the analyst or technician making the entry. These notebooks include, for example, instrument use and maintenance/calibration logs, pH logs, sample moisture determination logs, and sample receipt logs.

Recordkeeping for sample receipt is discussed under the Sample Management Section 5.1.

8.2.2 Standards

A bound logbook is maintained for all analytical reference materials used for USATHAMA work. The record includes the date of receipt, preparer, source, purity, composition, storage requirements, and expiration date, if applicable. Characterization data for purchased reference material is also included.

The preparation of working standards from reference materials is recorded in a bound logbook. This logbook may be of general use by several analysts for USATHAMA standards preparation, or an individual analyst's notebook, as for preparation of standards used for a single analytical run associated with a single lot of samples.

8.2.3 Instrument

Instrument maintenance records and, where applicable, instrument tuning and calibration data, are maintained in instrument specific logbooks. Actual analytical conditions pertaining to an individual lot analysis are recorded in the analyst's notebook, along with other pertinent analytical information.

8.3 Hard-Copy Output

Hard-copy output, (e.g., chromatograms and computer generated data evaluations) is labeled with date, time (where applicable), analytical method, sample numbers, the name or initials of the analyst generating the output, and other pertinent information. Storage of hard-copy output is with related analytical data pertaining to an individual lot analysis. All such data, comprising a complete record of an analysis, are compiled into one or more envelopes for archiving. The envelopes are properly labeled with the lot designation, method of analysis, matrix, analyst, analyst's notebook, and date of completion. When samples from multiple sites or projects are grouped together in a single lot, the data pertaining to each site are compiled (or copied) and stored separately, as directed by USATHAMA. All copies indicate the location of the original data.

8.4 Data Package Preparation

In general, all data should be maintained in two separate locations, the data package and the laboratory notebook(s).

Records to be contained in the data package should include, but are not limited to the following:

- Optimized instrumental conditions
- Original chromatograms, strip charts, and/or other instrument output
- Original chain-of-custody form and carrier transmittal documents
- All hardcopy GC/MS outputs
- Expanded scale blow-up of manually integrated peak(s).
- All data sheets or other pre-printed forms used by the contractor or laboratory.
- Copies of all relevant notebook pages. This should include preparation of standards, calibration, sample preparation/extraction, moisture determinations, calculations, and any other relevant comments.

Each data package should contain all information related to one lot for one installation. In cases where a lot has samples from more than one installation, then the information should be copied and placed in separate packages for each installation. In those packages which receive copies, the location of the original material should be identified.

Each data package should contain a contents and approval checklist. This should identify all materials which must be placed into the data package. This list should also list reviewer's names, dates of review, provide space for comments, notes, and corrective actions.

9.0
AUDITS

DCL facilities are always available for any required audits, announced or unannounced, by USATHAMA representatives.

The DCL Quality Assurance Coordinator conducts internal audits of critical functions within the laboratory, including verification that record keeping procedures are adequate, verification that general good laboratory practices, analytical methods and standard operating procedures are being followed, and continual assessment of quality control sample results. A summary of such audits is available for review at the laboratory. Internal audits shall be conducted by DCL QA personnel at a minimum rate of twice per month.

10.0
CORRECTIVE ACTION

When, as a result of audit procedures or the analysis of quality control samples, the analytical or other laboratory systems are found to be unsatisfactory, a corrective action is initiated. The unsatisfactory situation may be either immediate or long term in nature. Immediate short term problems may include unsatisfactory performance on quality control samples (which may be more involved than simply out-of-control data), errors or omissions in the compilation of the data package, or other problems peculiar to a single lot of samples. Long-term problems include trends or cycles in quality control sample analysis data, standard and solution preparation control, staff training in analytical and quality control procedures, or other problems which affect several analytical methods or multiple lots of samples.

To enhance the timeliness of corrective action and thereby reduce the generation of unacceptable data, problems identified by assessment procedures are resolved at the lowest possible management level. Problems that cannot be resolved at this level are reported to the Quality Assurance Coordinator (QAC) for resolution. The QAC determines the management level at which the problem can best be resolved, and notifies the appropriate manager. Weekly progress reports detail all problems and subsequent resolutions.

Steps included in the corrective action system include:

1. Defining the problem;
2. Assigning responsibility for problem investigation;
3. Investigating and determining the cause of the problem;
4. Assigning responsibility for problem resolution; and
5. Verifying that the resolution has corrected the problem.

Problems requiring corrective action may not be easy to identify or define. The situation may not be producing out-of-control data, but simply producing data not of the quality desired. The project manager, section managers, analysts, and the quality assurance staff combine efforts in solving long-term unsatisfactory situations.

All corrective actions are documented by Quality Assurance. Final corrective action reports, which relate to a particular lot analysis, are included in the data package for that lot.

11.0
QUALITY CONTROL REPORTS

DCL provides weekly quality assurance evaluation reports to USATHAMA, in conjunction with weekly interim technical reports from project management. The QA reports include charts and tables of quality control data, a control chart checklist delineating contracts and lots, and copies of Corrective Action Reports (CARs). These CARs include explanations of analytical or quality control problems and discussions of the corrective actions taken to alleviate those problems. Observations of data trends or situations which could develop into problems are also discussed in this report, as well as preliminary acceptance or rejection of analytical data.

APPENDIX A

APPENDIX A

LACK OF FIT AND ZERO INTERCEPT TESTS

B.1 LACK OF FIT TEST FOR CALIBRATION CURVES AND CERTIFICATION DATA

For most routinely used analytical systems, the instrument response is assumed to be a linear function of analyte concentration. The linear model can be tested by analyzing standards that have been prepared in replicate at each concentration. In addition to the calibration data (target versus instrument response), certification data (target versus found) is also subjected to the Lack of Fit (LOF) test. The usual method of least squares fitting assumes no error in the concentrations of standards.

There are two distinct linear first-order regression models that are generally encountered in analytical calibration. The non-zero intercept model is the most familiar, given by:

$$Y = Y_o + bX$$

where:

Y = Dependent Variable (Instrument Response or Found Concentration);

Y_o = Y Axis Intercept;

b = Slope of the Line; and

X = Target Concentration.

The estimates Y_o and b are calculated to minimize the Sum of Squares (SS) of the deviations from the line without restrictions. For some analyses, however, theory predicts that the response of the instrument should be linear with concentration and should also be zero when there is no analyte present. Thus, if the instrument has been calibrated correctly, the calculated line should pass through the origin by definition. The proper regression model would then be the Zero Intercept model:

$$\hat{Y} = b_o X$$

where:

$\hat{Y}$ = Predicted Value of Dependent Variable;

b_o = Slope of Line Through Origin; and

X = Target Concentration.

The estimate of b_o is calculated to minimize the SS of deviations from the line with the restriction that the line must pass through the origin.

For the model with an intercept:

$$b = \frac{N\sum X_i Y_i - \sum X_i \sum Y_i}{N\sum X_i^2 - (\sum X_i)^2} \qquad Y_o = \frac{\sum Y_i - b\sum X_i}{N}$$

For the model through the origin:

$$b_o = \frac{\sum X_i Y_i}{\sum X_i^2} \qquad Y_o = 0$$

where:

N = Number of Data Points;

X_i = i-th Target Concentration; and

Y_i = i-th Value of Dependent Variable.

The correlation coefficient is a measure of the relationship between two independent variables. In calibration and certification problems, it is assumed that a definite functional relationship exists between the dependent (response or found concentration) and independent (target concentration) variables. Therefore, the correlation coefficient is an insensitive tool for evaluating the quality of the fitted equation.

A more sensitive tool for evaluating the fitted equation is a regression analysis, in which the sources of variation are fractionated into the SS attributable to regression and the SS for residuals. When replicate measurements have been made, the residual SS can be separated into a systematic error component and a random error component. The SS due to systematic error is designated the SS due to LOF because it arises from the inadequacy of the fitted regression model to describe the experimental points.

For the model with intercept, the equation for calculating the SS of residuals is:

$$\text{SS Residual} = \left[\sum Y^2 - \frac{(\sum Y)^2}{N} \right] - b^2 \left[\sum X^2 - \frac{(\sum X)^2}{N} \right]$$

where:

Y = Values of Dependent Variable;

X = Target Concentration;

N = Total Number of Measurements; and

b = Slope of Best Fit Line.

The number of degrees of freedom (df) is N - 2, because two regression coefficients were fitted (slope and Y-axis intercept).

The SS for random error is independent of the regression model employed, depending only on the distribution of replicates around the mean at each concentration. When duplicate measurements have been acquired at each concentration, the SS for random error is given by:

$$\text{SS Random Error} = \frac{\sum d^2}{2}$$

where:

d = Difference in Values for Each Set of Duplicates.

The total df in this error estimate would be equal to the number of duplicates sets because each would contribute 1 df (2 - 1 = 1). When more than two replicates measurements are made, the SS random error for each set is given by:

$$\text{SS Random Error} = \sum Y^2 - \frac{(\sum Y)^2}{n}$$

where:

n = Number of Replicates in Each Set (df is n - 1).

Both the SS random error and the df are then summed across all sets to get the total SS random error and the total df.

After the total SS random error has been calculated, the SS for LOF can be obtained by difference according to:

SS LOF = (SS Residual) - (Total SS Random Error)

Similarly, the df associated with LOF is given by:

df LOF = (df Residual) - (df Total Random Error)

Regression analysis tables are used to determine whether the data fit the linear models and which linear model is more appropriate. The tables are calculated as shown in Table A-1. For calibration curves and certification data, the replicate analyses of the blank (zero concentration) are not used to obtain regression equations.

After calculating the regression analysis table, the F-ratio for LOF is compared to an F Table (Table A-2) to determine if the regression model is an adequate description of the data. The df LOF is used as v_1, df random error for v_2, and 95 percent confidence level. If the calculated F-ratio exceeds the value in the table, there is statistically significant LOF and the data are not linear.

The nature of this test is such that large random error will mask nonlinearity in the data. Very small random error can cause very small (and possibly unimportant) nonlinearity to be found significant (e.g., significant LOF). In fact, when random error is large (or very small), it is difficult to detect systematic variations that might cause LOF.

Table A.1. Regression Analysis Table for Model with Intercept

Source of Variation	Sum of Square (SS)	Degrees of Freedom (df)	Mean Square (MS)	F-Ratio
Residual	$\left[\Sigma Y^2 - \frac{(\Sigma Y)^2}{N}\right] - b^2\left[\Sigma X^2 - \frac{(\Sigma X)^2}{N}\right]$	N-2	$\frac{\text{Residual SS}}{N-2}$	-
Individual Error (for each set of data at each concentration)	$\Sigma Y^2 - \frac{(\Sigma Y)^2}{n}$ (for duplicates -- $\frac{\Sigma d^2}{2}$)	n-1	-	-
Total Error	Σ Individual Error SS	Σ df for Individual Error	$\frac{\text{Total Error SS}}{\text{df Total Error}}$	-
Lack of Fit (LOF)	Residual SS - Total Error SS	df Residual - df Total Error	$\frac{\text{LOF SS}}{\text{df LOF}}$	$\frac{\text{MS LOF}}{\text{MS Total Error}}$

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where Y = Values for Dependent Variable
X = Target Concentration
N = Total Number of Measurement
n = Number of Replicates at each Concentration
d = Difference between Duplicates

Do not round off intermediate numbers in calculations. Carry through at least six digits to avoid rounding off errors, even though in the final results less than six digits will be significant.

Table A.2. F-Ratio Critical Values (From Scheffe, 1959)

THE ANALYSIS OF VARIANCE

UPPER α POINT* OF F WITH ν_1 AND ν_2 D.F.

$\alpha = 0.05$

ν_2 \ ν_1	1	2	3	4	5	6	7	8	9
1	161	200	216	225	230	234	237	239	241
2	18.5	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4
3	10.1	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02
11	4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65
15	4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54
17	4.45	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46
19	4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39
21	4.32	3.47	3.07	2.84	2.68	2.57	2.49	2.42	2.37
22	4.30	3.44	3.05	2.82	2.66	2.55	2.46	2.40	2.34
23	4.28	3.42	3.03	2.80	2.64	2.53	2.44	2.37	2.32
24	4.26	3.40	3.01	2.78	2.62	2.51	2.42	2.36	2.30
25	4.24	3.39	2.99	2.76	2.60	2.49	2.40	2.34	2.28
26	4.23	3.37	2.98	2.74	2.59	2.47	2.39	2.32	2.27
27	4.21	3.35	2.96	2.73	2.57	2.46	2.37	2.31	2.25
28	4.20	3.34	2.95	2.71	2.56	2.45	2.36	2.29	2.24
29	4.18	3.33	2.93	2.70	2.55	2.43	2.35	2.28	2.22
30	4.17	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21
40	4.08	3.23	2.84	2.61	2.45	2.34	2.25	2.18	2.12
60	4.00	3.15	2.76	2.53	2.37	2.25	2.17	2.10	2.04
120	3.92	3.07	2.68	2.45	2.29	2.17	2.09	2.02	1.96
∞	3.84	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88

* Rounded off to three significant figures from tables of M. Merrington and C. M. Thompson in *Biometrika*, Vol. 33, pp. 78–87, 1943. Reproduced with the kind permission of the authors and the editor.

A.2 ZERO INTERCEPT TEST FOR CALIBRATION CURVES AND CERTIFICATION DATA

If the linear model with intercept is acceptable, the intercept must be tested to determine if it is significantly different from zero. The expression for calculating the slope of the line through the origin is:

$$b_o = \frac{\sum X_i Y_i}{\sum X_i^2}$$

Before testing the hypothesis that the intercept is zero, a regression analysis table is constructed (Table A-3). If the LOF for the model through the origin is not statistically significant, the Zero Intercept hypothesis is tested using the differences between the residual SS for the intercept and origin models.

To test the hypothesis that the intercept does not differ significantly from zero, calculate:

$$F = \frac{\text{SS Residual for Zero Intercept Model} - \text{SS Residual of Model with Intercept}}{\text{MS Residual of Model with Intercept}}$$

The df in the numerator will always be 1 because (N - 1) - (N - 2) = 1 and, therefore, the difference in these SS are divided by 1 to get the MS. The df in the denominator is N - 2.

The calculated F-ratio is compared to the critical values of F in Table A-2, at $v_1 = 1$ and $v_2 = N - 2$. If the calculated F-ratio is less than the critical value, the Zero Intercept model is accepted.

Generally, certification data will be expected to have intercepts not statistically different from zero. The procedures for daily calibration assume that the zero intercept model can be accepted. If intercepts are statistically different from zero, more rigorous calibration controls will be required and will be specified on a case-by-case basis in the project QC plan.

Table A.3. Regression Analysis Table for Model Through the Origin

Source of Variation	Sum of Square (SS)	Degrees of Freedom (df)	Mean Square (MS)	F-Ratio
Residual	$\Sigma Y^2 - \frac{(\Sigma XY)^2}{\Sigma X^2}$	N-1	$\frac{\text{Residual SS}}{\text{N-1}}$	-
Individual Error (for each set of data at each concentration)	$\Sigma Y^2 - \frac{(\Sigma Y)^2}{n}$ (for duplicates -- $\frac{\Sigma d^2}{2}$)	n-1	-	-
Total Error	Σ Individual Error SS	Σ df for Individual Error	$\frac{\text{Total Error SS}}{\text{df Total Error}}$	-
Lack of Fit (LOF)	Residual SS - Total Error SS	df Residual - df Total Error	$\frac{\text{LOF SS}}{\text{df LOF}}$	$\frac{\text{MS LOF}}{\text{MS Total Error}}$

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where Y = Values for Dependent Variable
X = Target Concentration
N = Total Number of Measurement
n = Number of Replicates at each Concentration
d = Difference between Duplicates

Do not round off intermediate numbers in calculations. Carry through at least six digits to avoid rounding off errors, even though in the final results less than six digits will be significant.

APPENDIX B

DATA CHEM LABORATORIES

USATHAMA ANALYTE SUMMARY
INORGANIC

		SOIL							WATER						
USATHAMA Analyte	Analyte Code	Amount Sample Needed	Container And Fixative/ (Solvent)	HOLD TIMES Extr./ Analysis	METHOD INSTR.	Certified Method #	CRL (µg/g)	Comments	Amount Sample Needed	Container And Fixative/ (Solvent)	HOLD TIMES Extr./ Analysis	METHOD INSTR.	Certified Method #	CRL (µg/L)	Comments
ARSENIC As	AS	10 g	20 mL Polyeth. Vial	-/180	GFAA	B9	2.5		500 mL	Plastic 0.5 mL HNO_3	-/180	GFAA	AX8	2.35	
HEX CHROMIUM Cr+6	CRHEX	10 g	4 oz. w/m Plastic	-/24 hrs.	Auto Analyzer	JY03	1.0		125 mL	Plastic	-/24 hrs.	Auto Analyzer	SF01	2.5	
IRON Fe	FE2	CERTIFICATION NOT REQUIRED							500 mL	Plastic	-/7	Spec	SY04	50.0	
LEAD Pb	PB	10 g	20 mL Polyeth. Vial	-/180	GFAA	JD21	0.467		250 mL	Plastic 0.5 mL HNO_3	-/180	GFAA	SD18	4.47	
MAGNESIUM Mg	MG	10 g	20 mL Polyeth. Vial	-/180	FLAA	JA02	2.37		250 mL	Plastic 0.5 mL HNO_3	-/180	FLAA	SC07	8.35	
MERCURY Hg	HG	10 g	20 mL Polyeth. Vial	-/28	CV	Y9	0.05		500 mL	Plastic 0.5 mL HNO_3	-/28	CV	CC8	0.10	
SELENIUM Se	SE	10 g	20 mL Polyeth. Vial	-/180	GFAA	JD20	0.449		250 mL	Plastic 0.5 mL HNO_3	-/180	GFAA	SD25	2.53	
SILVER Ag	AG	10 g	20 mL Polyeth. Vial	-/180	GFAA	JD22	0.0124		250 mL	Plastic 0.5 mL HNO_3	-/180	GFAA	SD26	0.333	
VANADIUM V	V	10 g	20 mL Polyeth. Vial	-/180	GFAA	JD23	0.941		500 mL	Plastic 0.5 mL HNO_3	-/180	GFAA	SD29	4.38	
AMMONIA	NH3N2	CERTIFICATION NOT REQUIRED							125 mL	Plastic 0.5 mL H_2SO_4	-/28	Auto Analyzer	TF30	8.42	
ANIONS Bromide* Fluoride Chloride Sulfate	Br F CL SO4	5 g	20 mL Polyeth. Vial	-/28	Ion Chrom.	KT07	Br 5.0 F 6.36 CL 7.12 SO4 5.0		125 mL	Plastic	-/28	Ion Chrom.	TT09	Br 407. F 153. CL 276. SO4 175.	
CYANIDE	CYN	10 g	4 oz. w/m Plastic	-/14	Auto Analyzer	KF15	0.25		250 mL	Plastic 1.0 mL NaOH	-/14	Auto Analyzer	TF34	5.0	
NITRATE/NITRITE	NIT	10 g	4 oz. w/m Plastic	-/28	Auto Analyzer	KF17	1.00		125 mL	Plastic 0.5 mL H_2SO_4	-/28	Auto Analyzer	LL8	10.0	
NITRITE	NO2	CERTIFICATION NOT REQUIRED							125 mL	Plastic	-/48 hrs.	Auto Analyzer	TF31	5.0	
NITROCELLULOSE	NC	10 g	4 oz. w/m Plastic	-/28	Auto Analyzer	LF05	23.1		125 mL	Plastic	-/28	Auto Analyzer	UF05	222	
T-PHOSPHORUS	P4	10 g	4 oz. w/m Plastic	-/28	Auto Analyzer	KF18	41.6		125 mL	Plastic 0.5 mL H_2SO_4	-/28	Auto Analyzer	TF29	1.0	
TKN	N2KJEL	CERTIFICATION NOT REQUIRED							125 mL	Plastic 0.5 mL H_2SO_4	-/28	Auto Analyzer	TF28	64.0	
SULFIDE	S	CERTIFICATION NOT REQUIRED							125 mL	Plastic 1 mL ZnAc 1 mL NaOH	-/7	Spec	TY15	11.0	Preservatives added to samples sequentially

APPENDIX B

DATA CHEM LABORATORIES

USATHAMA ANALYTE SUMMARY
INORGANIC

		SOIL							WATER						
USATHAMA Analyte	Analyte Code	Amount Sample Needed	Container And Fixative/ (Solvent)	HOLD TIMES Extr./ Analysis	METHOD INSTR.	Certified Method #	CRL (µg/g)	Comments	Amount Sample Needed	Container And Fixative/ (Solvent)	HOLD TIMES Extr./ Analysis	METHOD INSTR.	Certified Method #	CRL (µg/L)	Comments
ICP METALS I		10 g	20 mL Polyeth. Vial	-/180	ICP Sequent.	P9		RMA Analytes	500 mL	Plastic 0.5 mL HNO_3	-/180	ICP Sequent.	GG8		RMA Analytes
Cadmium	CD						CD 0.74							CD 8.4	
Calcium	CA						- -							CA 500.0	
Chromium	CR						CR 6.5							CR 24.0	
Copper	CU						CU 4.7							CU 26.0	
Lead	PB						PB 8.4							PB 74.0	
Magnesium	MG						- -							MG 500.0	
Potassium	K						- -							K 250.0	
Sodium	NA						- -							NA 940.0	
Zinc	ZN						ZN 8.7							ZN 22.0	
ICP METALS II		10 g	20 mL Polyeth. Vial	-/180	ICP Simultan.	JS12		CLASS Analytes	500 mL	Plastic 0.5 mL HNO_3	-/180	ICP Simultan.	SS12		CLASS Analytes
Aluminum	AL						AL 11.2							AL 112	
Antimony	SB						SB 19.6							SB 60.0	
Arsenic	AS						AS 16.4							AS 117	
Barium	BA						BA 3.29							BA 2.82	
Beryllium	BE						BE 0.427							BE 1.12	
Boron	B						B 6.64							B 230	
Cadmium	CD						CD 1.20							CD 6.78	
Calcium	CA						CA 25.3							CA 105	
Chromium	CR						CR 1.04							CR 16.8	
Cobalt	CO						CO 2.50							CO 25.0	
Copper	CU						CU 2.84							CU 18.8	
Iron	FE						FE 6.66							FE 77.5	
Lead	PB						PB 7.44							PB 43.4	
Magnesium	MG						MG 10.1							MG 135	
Manganese	MN						MN 9.87							MN 9.67	
Molybdenum	MO						MO 14.3							MO 52.7	
Nickel	NI						NI 2.74							NI 32.1	
Potassium	K						K 131							K 1240	
Selenium	SE						SE 20.7							SE 97.1	
Silver	AG						AG 0.803							AG 10.0	
Sodium	NA						NA 38.7							NA 279	
Tellurium	TE						TE 14.9							TE 118	
Thallium	TL						TL 34.3							TL 125	
Tin	SN						SN 7.43							SN 59.9	
Vanadium	V						V 1.41							V 27.6	
Zinc	ZN						ZN 2.34							ZN 16.0	

DATA CHEM LABORATORIES

USATHAMA ANALYTE SUMMARY
ORGANIC

		SOIL							WATER						
USATHAMA Analyte	Analyte Code	Amount Sample Needed	Container And Fixative/ (Solvent)	HOLD TIMES Extr./ Analysis	METHOD INSTR.	Cert. Method	CRL (µg/g)	Comments	Amount Sample Needed	Container And Fixative/ (Solvent)	HOLD TIMES Extr./ Analysis	METHOD INSTR.	Cert. Method	CRL (µg/L)	Comments
DBCP	DBCP	10 g	40 mL VOA Vial	7/40	GC/EC	89	0.005		1 Liter	Amber Glass with TFE Cap	7/40	GC/EC	AY8	0.20	
DMP	DMP	CERTIFICATION NOT REQUIRED							1 Liter	Amber Glass with TFE Cap	7/40	GC/FPD	AW8A	0.85	
DIMP/DMMP (Phosphonates)	DIMP DMMP	CERTIFICATION NOT REQUIRED							1 Liter	Amber Glass with TFE Cap	7/40	GC/FPD	AT8	DIMP 0.392 DMMP 0.188	
EXPLOSIVES HMX RDX Nitrobenzene Tetryl 1,3,5-Trinitrobenzene 1,3-Dinitrobenzene 2,4,6-Trinitrotoluene 2,4-Dinitrotoluene 2,6-Dinitrotoluene	 HMX RDX NB TETRYL 135TNB 13DNB 246TNT 24DNT 26DNT	10 g	4 oz. w/m Amber Glass w/TFE Cap	7/40	HPLC	LW23	HMX 2.00 RDX 1.28 NB 1.14 TETRYL 2.11 135TNB 0.822 13DNB 0.504 246TNT 2.00 24DNT 2.80 26DNT 2.00		1 Liter	Amber Glass with TFE Cap	7/40	HPLC	UW25	HMX 0.533 RDX 0.416 NB 0.662 TETRYL 0.631 135TNB 0.210 13DNB 0.456 246TNT 0.426 24DNT 0.397 26DNT 0.600	
HERBICIDES 2,4-D 2,4,5-T 2,4,5-TP	 24D 245T SILVEX	20 g	4 oz. w/m Amber Glass w/ TFE Cap	7/40	GC/EC	LH18	24D 0.0300 245T 0.0201 SILVEX 0.0356		1 Liter	Amber Glass with TFE Cap	7/40	GC/EC	UH10	24D 0.263 245T 0.180 SILVEX 0.095	
HYDRAZINES Hydrazine Monomethylhydrazine UDMH	 HYDRZ MHYDRZ UDMH	CERTIFICATION NOT REQUIRED							2 x 40 mL	40 mL VOA Vial w/o Septum	7/40	GC/NP	ZZ8	HYDRZ 30.8 MHYDRZ 2,970. UDMH 21.8	
HYDROCARBONS Methyl Isobutyl Ketone Dicyclopentadiene Bicycloheptadiene	 MIBK DCPD BCHPD	25 g	4 oz. w/m Amber Glass w/ TFE Cap ($MeCl_2$)	7/40	GC/FID	PP9	MIBK 0.64 DCPD 0.45 BCHPD 1.10		1 Liter	Amber Glass with TFE Cap	7/40	GC/FID	P8	MIBK 4.90 DCPD 4.98 BCHPD 5.87	
NITROGEN/ PHOSPHORUS PESTICIDES Atrazine Parathion Malathion Supona Vapona	 ATZ PRTHN MLTHN SUPONA DDVP	20 g	4 oz. w/m Amber Glass w/TFE Cap (Acetone/Hex.)	7/40	GC/EC	LH15	ATZ 0.161 PRTHN 0.159 MLTHN 0.126 SUPONA 0.146 DDVP 0.060		1 Liter	Amber Glass with TFE Cap	7/40	GC/EC	UH11	ATZ 4.03 PRTHN 0.647 MLTHN 0.373 SUPONA 0.787 DDVP 0.384	

DATA CHEM LABORATORIES

USATHAMA ANALYTE SUMMARY
ORGANIC

	SOIL							WATER						
USATHAMA Analyte	Analyte Code	Amount Sample Needed	Container And Fixative/ (Solvent)	HOLD TIMES Extr./ Analysis	METHOD INSTR.	Cert. Method	CRL (µg/g)	Comments	Amount Sample Needed	Container And Fixative/ (Solvent)	HOLD TIMES Extr./ Analysis	METHOD INSTR.	Cert. Method	CRL (µg/L)	Comments
NITROGLYCERIN/PETN		10 g	4 oz. w/m Amber Glass w/TFE Cap	7/40	HPLC/ DAD	LW27			1 Liter	Amber Glass with TFE Cap	7/40	HPLC/DAD	UW27		
Nitroglycerin	NG						NG 0.510							NG 1.48	
PETN	PETN						PETN 1.00							PETN 2.00	
NITROGUANIDINE	NQ	10 g	4 oz. w/m Amber Glass w/TFE Cap	7/40	HPLC/ DAD	LW30	0.0434		1 Liter	Amber Glass with TFE Cap	7/40	HPLC/DAD	UW29	21.1	
NITROSAMINES		2 x 10 g	40 mL VOA Vial w/o Septum (Methanol)	7/40	GC/NPD	LN08			1 Liter	Amber Glass with TFE Cap	7/40	GC/NPD	UN10		
Nitrosodimethylamine	NNDMEA						NNDMEA 0.010							NNDMEA 0.101	
Nitrosodipropylamine	NNDNPA						NNDNPA 0.0552							NNDNPA 1.80	
Nitrosodiphenylamine	NNDPA						NNDPA 0.060							NNDPA 1.93	
													(UN01)*	(NNDMEA 0.0421) (NNDNPA 0.117)	*Do not use without consulting R. Goebel
ORGANOCHLORINE PESTICIDES I		50 g	4 oz. w/m Amber Glass w/TFE Cap (Acetone/Hex.)	7/40	GC/EC	LH17		FOR ALL NON-RMA WORK	1 Liter	Amber Glass with TFE Cap	7/40	GC/EC	UH20		FOR ALL NON-RMA WORK
Aldrin	ALDRN						ALDRN 0.0014							ALDRN 0.0074	
Alpha-BHC	ABHC						ABHC 0.0028							ABHC 0.0026	
Beta-BHC	BBHC						BBHC 0.0077							BBHC 0.0099	
Delta-BHC	DBHC						DBHC 0.0085							DBHC 0.0034	
Lindane	LIN						LIN 0.0010							LIN 0.0025	
Chlordane	CLDAN						CLDAN 0.0884							CLDAN 0.0312	
Dieldrin	DLDRN						DLDRN 0.0016							DLDRN 0.0074	
Endrin	ENDRN						ENDRN 0.0085							ENDRN 0.0176	
Endrin Aldehyde	ENDRNA						ENDRNA –							ENDRNA 0.0504	
Endosulfan I	AENSLF						AENSLF 0.0010							AENSLF 0.0025	
Endosulfan II	BENSLF						BENSLF 0.0007							BENSLF 0.0077	
Isodrin	ISODR						ISODR 0.0030							ISODR 0.0025	
Methoxyclor	MEXCLR						MEXCLR 0.0359							MEXCLR 0.0750	
Heptachlor	HPCL						HPCL 0.0022							HPCL 0.0025	
Heptachlor Epoxide	HPCLE						HPCLE 0.0013							HPCLE 0.0063	
p,p'-DDE	PPDDE						PPDDE 0.0027							PPDDE 0.0039	
p,p'-DDD	PPDDD						PPDDD 0.0027							PPDDD 0.0061	
p,p'-DDT	PPDDT						PPDDT 0.0036							PPDDT 0.0025	
PCB-1016	PCB016						PCB016 0.100							PCB016 0.365	
PCB-1221	PCB221						--							--	
PCB-1232	PCB232						--							--	
PCB-1242	PCB242						--							--	
PCB-1248	PCB248						--							--	
PCB-1254	PCB254						--							--	
PCB-1260	PCB260						PCB260 0.0479							PCB260 0.176	
Toxaphene	TXPHEN						TXPHEN 0.226							TXPHEN 1.64	

DATA CHEM LABORATORIES

USATHAMA ANALYTE SUMMARY
ORGANIC

		SOIL							WATER						
USATHAMA Analyte	Analyte Code	Amount Sample Needed	Container And Fixative/ (Solvent)	HOLD TIMES Extr./ Analysis	METHOD INSTR.	Cert. Method	CRL (µg/g)	Comments	Amount Sample Needed	Container And Fixative/ (Solvent)	HOLD TIMES Extr./ Analysis	METHOD INSTR.	Cert. Method	CRL (µg/L)	Comments
ORGANOCHLORINE PESTICIDES II		50 g	4 oz. w/m Amber Glass w/TFE Cap (Acetone/Hex.)	7/40	GC/EC	KK9B		FOR USE AT RMA ONLY	1 Liter	Amber Glass w/TFE Cap	7/40	GC/EC	KK8		FOR USE AT RMA ONLY
Aldrin	ALDRN						ALDRN 0.00211							ALDRN 0.050	
Chlordane	CLDAN						CLDAN 0.0230							CLDAN 0.095	
Dieldrin	DLDRN						DLDRN 0.00181							DLDRN 0.050	
DDE	PPDDE						PPDDE 0.00486							PPDDE 0.054	
DDT	PPDDT						PPDDT 0.00277							PPDDT 0.049	
Endrin	ENDRN						ENDRN 0.00471							ENDRN 0.050	
Hexachlorocycl.	CL6CP						CL6CP 0.00137							CL6CP 0.048	
Isodrin	ISODR						ISODR 0.00186							ISODR 0.051	
ORGANOSULFUR COMPOUNDS		25 g	4 oz. w/m Amber Glass w/ TFE Cap ($MeCl_2$)	7/40	GC/FPD	LL06			1 Liter	Amber Glass with TFE Cap	7/40	GC/FPD	AAA8		
Dimethyldisulfide	DMDS						DMDS 0.802							DMDS 0.55	
1,4-oxathiane	OXAT						OXAT 1.80							OXAT 2.38	
1,4-dithiane	DITH						DITH 0.800							DITH 1.34	
Benzothiazole	BTZ						BTZ 5.18							CPMS 5.69	
CPMS	CPMS						CPMS 3.20							CPMSO 11.51	
CPMSO	CPMSO						CPMSO 13.8							CPMSO2 7.48	
CPMSO2	CPMSO2						CPMSO2 3.33							BTZ 5.00	
PHENOLS		25 g	4 oz. w/m Amber Glass w/ TFE Cap ($MeCl_2$)	7/40	GC/FID	LJ05			1 Liter	Amber Glass with TFE Cap	7/40	GC/FID	UJ05		
Phenols	PHENOL						PHENOL 0.202							PHENOL 1.28	
2-Chlorophenol	2CLP						2CLP 0.518							2CLP 9.85	
2-Nitrophenol	2NP						2NP 0.787							2NP 16.5	
2,4-Dimethylphenol	24DMPN						24DMPN 2.06							24DMPN 1.41	
2,4-Dichlorophenol	24DCLP						24DCLP 0.798							24DCLP 1.52	
4-Chloro-3-cresol	4CL3C						4CL3C 0.263							4CL3C 1.20	
2,4,5-Trichlorophenol	245TCP						245TCP 1.09							245TCP 2.38	
4-Nitrophenol	4NP						4NP 1.04							4NP 11.5	
4,6-Dinitro-2-cresol	46DN2C						46DN2C 62.4							46DN2C 350	
Pentafluorophenol	PFP						PFP 53.8							PFP 291	
Pentachlorophenol	PCP						PCP 3.51							PCP 39.8	
TETRAZENE	TETR	20 g	4 oz. w/m Amber Glass w/ TFE Cap (MeOH)	7/40	HPLC	LW28	1.84		250 mL	Amber Glass w/TFE Cap	-/40	HPLC	UW30	7.03	
THIODIGLYCOL		2 x 10 g	40 mL VOA Vial without Septum (Basic Methanol	7/40	HPLC/ DAD	LL9			1 Liter	Amber Glass w/ TFE Cap	7/40	HPLC/ DAD	AZ8		
Thiodiglycol	TDGCL						TDGCL 4.20							TDGCL 6.69	
Chloroacetic Acid	CLC2A						CLC2A 35.5								

DATA CHEM LABORATORIES

USATHAMA ANALYTE SUMMARY
ORGANIC

		SOIL							WATER						
USATHAMA Analyte	Analyte Code	Amount Sample Needed	Container And Fixative/ (Solvent)	HOLD TIMES Extr./ Analysis	METHOD INSTR.	Cert. Method	CRL (µg/g)	Comments	Amount Sample Needed	Container And Fixative/ (Solvent)	HOLD TIMES Extr./ Analysis	METHOD INSTR.	Cert. Method	CRL (µg/L)	Comments
VOLATILE HALOGENS		2 x 10 g	40 mL VOA Vial w/o Septum (Methanol)	7/14	P&T/GC	LG06		CH3CL AND C2H5CL ARE TO BE RECERTIFIED	2 x 40 mL	40 mL VOA Vial w/ Septum 4 drops 1:1 HCl	-/7	P&T/GC	UG06		
1,1,2,2-Tetrachloroethane	TCLEA						TCLEA 0.0260							TCLEA 0.250	
1,2-Dichlorobenzene	12DCLB						12DCLB 0.102							12DCLB 0.182	
1,3-Dichlorobenzene	13DCLB						13DCLB 0.0674							13DCLB 0.882	
1,4-Dichlorobenzene	14DCLB						14DCLB 0.0820							14DCLB 0.194	
1,2-Dichloropropane	12DCLP						12DCLP 0.0151							12DCLP 0.100	
2-Chloroethylvinylether	2CLEVE						2CLEVE 0.0500							2CLEVE 0.578	
Bromodichloromethane	BRDCLM						BRDCLM 0.147							BRDCLM 0.966	
Dibromochloromethane	DBRCLM						DBRCLM 0.0453							DBRCLM 0.252	
Chloromethane	CH3CL						CH3CL							CH3CL 5.46	
Bromomethane	CH3BR						CH3BR 0.544							CH3BR 3.71	
Bromoform	CHBR3						CHBR3 0.192							CHBR3 1.52	
cis-1,3-Dichloropropene	C13DCP						C13DCP 0.0106							C13DCP 0.618	
trans-1,3-Dichloropropene	T13DCP						T13DCP 0.0721							T13DCP 0.378	
Chloroethane	C2H5CL						C2H5CL							C2H5CL 2.72	
Vinyl Chloride	C2H3CL						C2H3CL 0.186							C2H3CL 4.91	
Trichlorofluoromethane	CCL3F						CCL3F 0.146							CCL3F 0.636	
Dichlorodifluoromethane	CCL2F2						CCL2F2 0.375							CCL2F2 24.4	
Carbon Tetrachloride	CCL4						CCL4 0.0271							CCL4 0.514	
Chlorobenzene	CLC6H5						CLC6H5 0.0310							CLC6H5 0.451	
Chloroform	CHCL3						CHCL3 0.456							CHCL3 0.635	
1,1-Dichloroethane	11DCLE						11DCLE 0.0823							11DCLE 0.306	
1,2-Dichloroethane	12DCLE						12DCLE 0.0167							12DCLE 1.07	
1,1-Dichloroethene	11DCE						11DCE 0.109							11DCE 0.500	
1,2-Dichloroethene	12DCE						12DCE 0.0959							12DCE 0.831	
Methylene Chloride	CH2CL2						CH2CL2 0.0637							CH2CL2 0.902	
Trichloroethene	TRCLE						TRCLE 0.0430							TRCLE 0.315	
Tetrachloroethene	TCLEE						TCLEE 0.0128							TCLEE 0.0857	
1,1,1-Trichloroethane	111TCE						111TCE 0.0167							111TCE 0.832	
1,1,2-Trichloroethane	112TCE						112TCE 0.0101							112TCE 0.100	
VOLATILE AROMATICS		2 x 10 g	40 mL VOA Vial w/o Septum (Methanol)	7/14	P&T/GC	AA9			2 x 40 mL	40 mL VOA Vial w/ Septum 4 drops 1:1 HCl	-/7	P&T/GC	AV8		
Benzene	C6H6						C6H5 0.065							C6H6 1.06	
Toluene	MEC6H5						MEC6H5 0.19							MEC6H5 1.47	
Ethylbenzene	ETC6H5						ETC6H5 0.16							ETC6H5 1.37	
1,3-Xylene	13DMB						13DMB 0.26							13DMB 1.32	
1,2 & 1,4-Xylene	XYLEN						XYLEN 0.39							XYLEN 1.36	
Chlorobenzene	CLC6H5													CLC6H5 1.39	
1,2-Dichlorobenzene	12DCLB													12DCLB 0.482	
1,3-Dichlorobenzene	13DCLB													13DCLB 0.566	
1,4-Dichlorobenzene	14DCLB													14DCLB 0.579	
GC/MS VOLATILES For analyte list see Page 7		2 x 10 g	40 mL VOA Vial (Methanol)	-/14	GC/MS	LM23	See Page 7		2 x 40 mL	40 mL VOA Vial w/Septum 4 drops 1:1 HCl	-/14	GC/MS	UM21	See Page 7	To remove res. Cl_2, add ascorbic acid.
GC/MS SEMI-VOLATILES For analyte list see Page 7		50 g	4 oz. w/m Amber Glass w/ TFE Cap ($MeCl_2$)	7/40	GC/MS	LM25	See Page 7		1 Liter	Amber Glass w/TFE Cap	7/40	GC/MS	UM25	See Page 7	

USATHAMA ANALYTE SUMMARY
GC/MS VOLATILES AND SEMIVOLATILES LIST

VOLATILES
Soil Method LM23 Water Method UM21

USATHAMA Analyte	Analyte Code	SOIL CRL (µg/g)	WATER CRL (µg/L)
1,1,1-Trichloroethane	111TCE	0.20	1.0
1,1,2,2-Tetrachloroethane	TCLEA	0.20	1.0
1,1,2-Trichloroethane	112TCE	0.33	1.0
1,1-Dichloroethane	11DCLE	0.49	1.0
1,1-Dichloroethene	11DCE	0.27	1.0
1,2-Dichlorobenzene	DCLB*	0.20	1.0
1,2-Dichloroethane	12DCLE	0.32	1.0
1,2-Dichloroethane-d4-S	12DCD4	0.50	1.0
1,2-Dichloroethene	12DCE	0.32	5.0
1,2-Dichloropropane	12DCLP	0.53	1.0
1,3-Dichlorobenzene	13DCLB	0.14	1.0
1,3-Dichloropropane	13DCP	0.20	4.8
1,4-Dichlorobenzene	DCLB*	0.20	0.10
2-Chloroethylvinyl Ether	2CLEVE	0.50	3.5
Benzene	C6H6	0.10	1.0
Bromodichloromethane	BRDCLM	0.20	1.0
Bromoform	CHBR3	0.20	11.0
Carbon Tetrachloride	CCL4	0.31	1.0
Chlorobenzene	CLC6H5	0.10	1.0
Chloroethane	C2H5CL	0.64	8.0
Chloroform	CHCL3	0.24	1.0
Chloromethane	CH3CL	0.86	1.2
Dibromochloromethane	DBRCLM	0.25	1.0
Ethylbenzene	ETC6H5	0.19	1.0
Ethylbenzene-d10-S	ETBD10	0.10	1.0
Methylene Chloride	CH2CL2	4.4	1.0
Methylene Chloride-d2-S	CDCL2	2.4	9.7
Tetrachloroethene	TCLEE	0.16	1.0
Toluene	MEC6H5	0.10	1.0
Toluene-d8-S	MEC6D5	0.10	1.0
Trichloroethene	TRCLE	0.23	1.0
Vinyl Chloride	C2H3CL	1.8	12.0
Acrylonitrile	ACRYLO	2.0	8.4
Trichlorofluoromethane	CCL3F	0.23	1.0
1,3-Dimethylbenzene	13DMB	0.23	1.0
1,2-Dimethylbenzene	XYLEN*	0.78	1.0
1,4-Dimethylbenzene	XYLEN*	0.78	1.0
Acetone	ACET	3.3	8.0
Methylethylketone	MEK	4.3	10.0
Methylisobutylketone	MIBK	0.63	1.4
Bromomethane	CH3BR	0.26	14.0

SEMIVOLATILES
Soil Method LM25 Water Method UM25

USATHAMA Analyte	Analyte Code	SOIL CRL (µg/g)	WATER CRL (µg/L)
4,4'-DDE	PPDDE	0.068	14
4,4'-DDT	PPDDT	0.10	18
Aldrin	ALDRN	1.3	13
Chlordane	CLDAN	0.68	37
Dieldrin	DLDRN	0.079	26
Dithiane	DITH	0.065	3.3
Endrin	ENDRN	1.3	18
2-Fluorophenol	2FP	0.18	22
Phenol-d6	PHEND6	0.089	34
2,4,6-Tribromophenol	246TBP	0.52	20
3,5-Dinitroaniline	35DNA	1.6	21
Terphenyl-d14	TRPD14	0.13	35
p-Chlorophenylmethyl Sulfide	CPMS	0.087	10
p-Chlorophenylmethyl Sulfone	CPMSO2	0.066	5.3
p-Chlorophenylmethyl Sulfoxide	CPMSO	0.32	15
Parathion	PRTHN	1.7	37
Phenol	PHENOL	0.052	2.2
2-Chlorophenol	2CLP	0.065	2.8
2-Nitrophenol	2NP	1.1	8.2
2,4-Dimethylphenol	24DMPN	3.0	4.4
2,4-Dichlorophenol	24DCLP	0.065	8.4
p-Chloro-m-cresol	4CL3C	0.93	8.5
4-Nitrophenol	4NP	3.3	96
Pentachlorophenol	PCP	0.76	9.1
1,4-Oxathiane	OXAT	0.075	27
Isodrin	ISODR	0.48	7.8
Vapona	DDVP	0.068	8.5
Supona	SUPONA	0.92	19
Atrazine	ATZ	0.065	5.9
Malathion	MLTHN	0.18	21
Hexachlorocyclopentadiene	CL6CP	0.52	54
2,4,5-Trichlorophenol	245TCP	0.49	2.8
2,3,6-Trichlorophenol	236TCP	0.62	1.6
2,4,6-Trichlorophenol	246TCP	0.081	3.6
2-Chlorophenol-d4-S	2CLPD4	0.35	14
1,3-Dichlorobenzene-d4-S	13DBD4	0.050	8.7
Diethyl Phthalate-d4-S	DEPD4	0.060	5.5
Dicyclopentadiene	DCPD	0.57	21
Dibromochloropropane	DBCP	0.071	12
Di-n-octylphthalate-d4	DNOPD4	0.065	13
Endrin Aldehyde	ENDRNA	1.8	5.0
2-Fluorobiphenyl	2FBP	0.057	17
Nitrobenzene-d5	NBD5	0.22	26
1,2,3-Trichlorobenzene	123TCB	0.032	5.8
1,2,4-Trichlorobenzene	124TCB	0.22	2.4
1,2-Dichlorobenzene	12DCLB	0.042	1.2
1,3-Dichlorobenzene	13DCLB	0.042	3.4
1,4-Dichlorobenzene	14DCLB	0.034	1.6
2,4-Dinitrotoluene	24DNT	1.4	5.8
2,6-Dinitrotoluene	26DNT	0.32	6.7
2-Chloronaphthalene	2CNAP	0.24	2.6
4,4'-DDD	PPDDD	0.064	18
Acenaphthalene	ANAPYL	0.033	5.1
Acenaphthene	ANAPNE	0.041	5.6
Alpha-BHC	ABHC	1.3	5.3
Anthracene	ANTRC	0.71	5.2
Benzo (a) Anthracene	BAANTR	0.041	9.6
Benzo (a) Pyrene	BAPYR	1.2	14
Benzo (b) Fluoranthene	BBFANT	0.31	10
Benzo (ghi) Perylene	BGHIPY	0.16	15
Benzo (k) Fluoranthene	BKFANT	0.13	10
Beta-BHC	BBHC	1.3	17
Bis (2-Chloroethyl) Ether	B2CLEE	0.36	0.66
Bis (2-Ethyl hexyl) Phthalate	B2EHP	0.48	7.7
Chrysene	CHRY	0.032	7.4
Delta-BHC	DBHC	0.21	—
Di-n-Octyl Phthalate	DNOP	0.23	1.4
Heptachlor	HPCL	0.24	38
Heptachlor Epoxide	HPCLE	0.48	28
Hexachlorobenzene	CL6BZ	0.080	12
Hexachlorobutadiene	HCBD	0.97	8.7
Indeno (1,2,3,cd) Pyrene	ICDPYR	2.4	21
Lindane (g-BHC)	LIN	0.10	7.2
N-Nitroso-Di-n-Propylamine	NNDNPA	1.1	6.9
Naphthalene	NAP	0.74	0.23
Phenanthrene	PHANTR	0.032	9.9
Pyrene	PYR	0.083	17
N-Nitrosodimethylamine	NNDMEA	0.46	9.7
N-Nitrosodiphenylamine	NNDPA	0.29	3.7
Dibenzo(a,h)Anthracene	DBAHA	0.31	12
Methoxychlor	MEXCLR	0.26	11
PCB-1016**	PCB016	0.32	—
PCB-1260**	PCB260	0.79	—
Endosulfan I	AENSLF	0.40	23
Endosulfan II	BENSLF	2.4	42
Toxaphene	TXPHEN	12.0	—
Fluorene	FLRENE	0.065	9.2
Mirex	MIREX	0.14	24
Cl6ET	Cl6ET	1.6	8.3
Hexachloroethane	Cl6ET	1.6	8.3
Dimethyl Phthalate	DMP	0.063	2.2
Diethyl Phthalate	DEP	0.24	5.9
Di-n-butyl Phthalate	DNBP	1.3	33
Butyl Benzyl Phthalate	BBZP	1.6	28
Isophorone	ISOPHR	0.39	2.4
Nitrobenzene	NB	1.6	3.7
Endosulfan Sulfate	ESFSO4	1.2	50
Bis (2-Chloroethoxy) Methane	B2CEOM	0.19	6.6
Bis (2-Chloroisopropyl) Ether	B2CIPE	0.44	5.0
4-Chlorophenyl Phenyl Ether	4CLPPE	0.17	23
4-Bromophenyl Phenyl Ether	4BRPPE	0.041	22
3,3'-Dichlorobenzidine	33DCBD	1.6	5.0
2,4-Dinitrophenol	24DNP	4.7	170
1,2-Diphenylhydrazine	12DPH	0.52	13
Fluoranthene	FANT	0.032	24
PCB-1262	PCB262	8.3	—
3-Nitrotoluene	3NT	0.34	2.9
3-Nitroaniline	3NANIL	3.0	15
2,6-Dinitroaniline	26DNA	0.57	8.6
4-Methylphenol	4MP	0.24	2.6
2-Methylphenol	2MP	0.096	3.6
2-Methylnaphthalene	2MNAP	0.032	1.3
Benzyl Alcohol	BZALC	0.032	4.0
Dibenzofuran	DBZFUR	0.36	5.1
4,6-Dinitro-2-Cresol	46DN2C	0.60	—
Diisopropylmethylphosphonate	DIMP	—	21
Dimethylmethylphosphonate	DMMP	—	130
Bromacil	BRMCIL	—	2.9

* 12DCLB and 14DCLB coelute as DCLB, and 1,2-Dimethylbenzene and 1,4-Dimethylbenzene coelute as XYLEN

** All other non-certified PCBs are based on the relative data for PCB-1016 and PCB-1260.

APPENDIX C

APPENDIX C

SAMPLE CONTAINER CLEANING PROCEDURES

To ensure the integrity of aqueous and solid samples, steps must be taken to minimize contamination from the containers in which they are stored. If the analyte(s) to be determined are organic in nature, the container should be made of amber glass. If the analyte(s) are inorganic, the container should be polyethylene. When both organic and inorganic substances are expected to be present, separate samples should be taken. New sample bottles must be cleaned according to either of the procedures presented below; reuse of sample containers is expressly prohibited. The procedure that was used must be documented. Commercially cleaned containers may be utilized if cleaning procedures comply with those provided in this appendix and prior USATHAMA Chemistry Branch approval is obtained. The procedures for cleaning the glass and polyethylene containers and their caps are as follows:

ALTERNATE A:

- Polyethylene Bottles and Polyethylene Caps

  (1) Rinse bottles and lids with 5 percent sodium hydroxide.

  (2) Rinse with deionized water.

  (3) Rinse with 5 percent Ultrex (or equivalent) nitric acid in deionized water.

  (4) Rinse with deionized water.

  (5) Drain and air dry.

- Amber-Glass Bottles or 40-ml Vials

  (1) Scrub and wash bottles in detergent.

  (2) Rinse with copious amounts of distilled water.

  (3) Rinse with acetone.

  (4) Rinse with methylene chloride (Nanograde or equivalent).

  (5) Rinse with hexane (Nanograde or equivalent).

  (6) Air dry.

(7) Heat to 200°C.

(8) Allow to cool.

(9) Cap with clean caps with Teflon liners.

- Bottle Caps

(1) Remove paper liners from caps.

(2) Wash with detergent.

(3) Rinse with distilled water.

(4) Dry at 40°C.

- Teflon Liners (avoid contact with fingers)

(1) Wash with detergent.

(2) Rinse with distilled water.

(3) Rinse with acetone.

(4) Rinse with hexane (Nanograde or equivalent).

(5) Air dry.

(6) Place liners in cleaned caps.

(7) Heat to 40°C for 2 hours.

(8) Allow to cool.

(9) Use to cap cleaned bottles.

ALTERNATE B: (Specified by EPA for CLP)

- Amber Glass Bottles

(1) Wash containers, closures, and teflon liners in hot tap water with laboratory grade non-phosphate detergent.

(2) Rinse three times with tap water.

(3) Rinse with 1:1 nitric acid.

(4) Rinse three times with ASTM Type 1 deionized water.

(5) Rinse with pesticide grade methylene chloride.

(6) Oven dry.

(7) Remove containers, closures, and teflon liners from oven.

(8) Place teflon liners in closures and place closures on containers. Attendant to wear gloves and containers not to be removed from preparation room until sealed.

- 40 mL Borosilicate Glass Vials

(1) Wash vials, septa, and closures in hot tap water with laboratory grade non-phosphate detergent.

(2) Rinse three times with tap water.

(3) Rinse three times with ASTM Type 1 deionized water.

(4) Oven dry vials, septa, and closures.

(5) Remove vials, septa, and closures from oven.

(6) Place septa in closures, teflon side down, and place on vials. Attendant to wear gloves and vials not to be removed from preparation room until sealed.

- High Density Polyethylene Bottles

(1) Wash bottles, closures, and teflon liners with hot tap water with laboratory grade non-phosphate detergent.

(2) Rinse three times with tap water.

(3) Rinse with 1:1 nitric acid.

(4) Rinse three times with ASTM Type 1 deionized water.

(5) Air dry in contaminant-free environment.

(6) Place liners in closures and place closures on bottles. Attendant to wear gloves and bottles not to be removed from preparation room until sealed.

Documentation must be provided to the USATHAMA Chemistry Branch validating that the bottles are in fact "clean." Documentation may consist of the results of "bottle blank" analysis using the method(s) that will be applied to the sample that will be placed in that bottle. QC results from the supplier of commercially cleaned containers, demonstrating that the bottle(s) are "clean," will be acceptable. The documentation must be provided before the bottles are used to collect samples in the field. This validation is to be performed or provided for each batch or "lot" of bottles cleaned together and must be provided at least once for each installation where they are used.

APPENDIX D

THIS LOT DIES
Extraction: _____
Analysis: _____

CHAIN OF CUSTODY RECORD
0000—USATHAMA Installation

RESULTS DUE TO CUSTOMER: _____

SAMPLE EXTRACTION DATE: _____

SAMPLE ANALYSIS DATE: _____

PROJECT/JOB/TASK	LOT	ANALYSIS

Date Sampled	Site ID	DCL Sample Number(s)	Sample Matrix	Depth (ft)	Field Sample Number	Moisture Lot	Remarks

Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)
Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)
Relinquished by: (Signature)	Date/Time	Received by: (Signature)	Relinquished by: (Signature)	Date/Time	Received by: (Signature)

Final Disposition: _____ Signature: _____

DataChem Laboratories/ 960 West LeVoy Drive / Salt Lake City, Utah 84123

REVISED 8/22/19

Appendix B: Checklist for Field and Laboratory Activities

FIELD CHECKLIST

Signature of Auditor _____ Date of Audit _____

Project Coordinator _____ Project No. _____

Project Location _____

Type of Investigation (Authority, Agency) _____

Briefing with Project Coordinator

Yes _ No _ N/A _ 1. Was a project plan prepared? If yes, what items are addressed in the plan?

_____
_____
_____

Yes _ No _ N/A _ 2. Were additional instructions given to project participants (i.e., changes in project plan)? If yes, describe these changes.

_____
_____
_____

Yes _ No _ N/A _ 3. Is there a written list of sampling locations and descriptions? If yes, describe where documents are.

_____
_____
_____

Yes _ No _ N/A _ 4. Is there a map of sampling locations? If yes, where is the map?

_____
_____
_____

Yes _ No _ N/A _ 5. Do the investigators follow a system of accountable documents? If yes, what documents are accountable?

_____
_____
_____

FIELD CHECKLIST

FIELD OBSERVATIONS

Yes _ No _ N/A _

1. Was permission granted to enter and inspect the facility (required if RCRA inspection)?

_____
_____
_____

Yes _ No _ N/A _

2. Is permission to enter the facility documented? If yes, where is it documented?

_____
_____
_____

Yes _ No _ N/A _

3. Were split samples offered to the facility If yes, was the offer accepted or declined?

_____
_____
_____

Yes _ No _ N/A _

4. Is the offering of split samples recorded? If yes, where is it recorded?

_____
_____
_____

Yes _ No _ N/A _

5. If the offer to split samples was accepted, were the split samples collected? If yes, how were they identified?

_____
_____
_____

Yes _ No _ N/A _

6. Are the number, frequency and types of field measurements, and observations taken as specified in the project plan or as directed by the project coordinator? If yes, where are they recorded?

_____
_____
_____

- Signatures and titles of persons involved in chain-of-possession; and
- Inclusive dates of possession for each possession.

Yes _ No _ N/A _

13. Does a sample analysis sheet accompany all samples on delivery to the laboratory sample custodian?

Yes _ No _ N/A _

14. At the minimum, has the following information been completed on each sample analysis request sheet?

- Name of person receiving sample (sample custodian);
- Laboratory sample number;
- Date of sample receipt;
- Sample allocation;
- Analyses to be performed;
- Collector's name, affiliattion name, address, and phone number;
- Date and time of sampling;
- Location of sampling; and
- Special handling and/or storage requirements.

Yes _ No _ N/A _

15. Has a field custodian been assigned for sample recovery, preservation, and storage until shipment?

Yes _ No _ N/A _

16. Where applicable, are sample collection containers rinsed three times with the sample material prior to collection?

QUALITY ASSURANCE/QUALITY CONTROL

SAMPLE DOCUMENTATION AND CHAIN-OF-CUSTODY

Yes _ No _ N/A _

1. Is the following information being recorded in the field log book or on data sheets?

- Project name and project number;
- Purpose of sampling (e.g., quarterly sampling, resample to confirm previous analysis, initial site assessment, etc.;
- Date and time each sample was collected;
- Date and starting/stopping times (Hr:Min) for air samples;
- Date and well bailing time for groundwater;
- Blank, duplicate and split sample identification numbers;
- Sample description including type (i.e., soil, sludge, groundwater, etc.);
- Field measurement results (i.e., conductivity, pH, dissolved oxygen, combustible gas (e.g., LEL), radioactivity, etc.);
- Preservation method for each sample;
- Type and quantity of containers used for each sample;
- Weather conditions at time of sampling;
- Photographic log identifying subject, reason for photograph, date, time, direction in which photograph was taken, number of the picture on the roll;
- Sample destination;
- Analyses to be performed on each sample;
- Reference number from all forms on which the sample is listed or labels attached to the sample (i.e., chain-of-custody, bill of lading or manifest forms, etc.);
- Name(s) of sampling personnel; and
- Signature of person(s) making entries on each page.

_____

_____

_____

_____

_____

_____

_____

_____

CHECKLIST FOR MECHANICALLY CORED SAMPLES

Yes _ No _ N/A _ 1. Was the rig set up at a staked and cleared borehole location?

Yes _ No _ N/A _ 2. Was the location, date, time, and other pertinent information recorded on boring log form?

Yes _ No _ N/A _ 3. Was polybutyrate core tubes cut to specification and placed into core barrel?

Yes _ No _ N/A _ 4. Was augering and coring conducted according to the following sequence: 0-1 ft, 1-4 ft, 4-5 ft, 5-9 ft, and 9-10 ft, etc.?

Yes _ No _ N/A _ 5. Was the core barrel removed from the borehole and opened at the completion of each coring interval?

Yes _ No _ N/A _ 6. Was the 12-inch sections for laboratory analysis removed, capped with Teflon film lined plastic caps, sealed with tape, and immediately placed in a cooler?

Yes _ No _ N/A _

13. Was the boring stake left in the ground adjacent to the borenole and a board placed over the hole until it was grouted?

Yes _ No _ N/A _

14. Were all boreholes greater than 1 ft in depth grouted the same day of construction and the borehole location stake placed in the grout?

Yes _ No _ N/A _

15. Were one foot deep borings backfilled with native materials available adjacent to the boring?

Yes _ No _ N/A _

16. Were the augers, and other downhole equipment decontaminated in the field prior to moving to the next borehole location upon completion of each boring?

Yes _ No _ N/A _

17. When all borings in a specific source were completed was the drill rig initially cleaned at the source location?

Yes _ No _ N/A _

18. Upon completion of the initial cleaning was the drill rig transported to the decontamination pad where it was thoroughly steam-cleaned before entering another source area?

CHECKLIST FOR HAND CORED SAMPLES

Yes _ No _ N/A _ 1. Was a piece of Teflon film and plywood placed over the top of the polybutyrate tube and the tube pushed or driven into the ground by hand?

Yes _ No _ N/A _ 2. Was the tube removed from the ground by shovel, the tube exterior wiped clean, the ends capped with Teflon film lined plastic caps, and sealed with tape?

Yes _ No _ N/A _ 3. Were the sample tubes marked with the boring number, the depth of the interval sampled, and the upward direction?

Yes _ No _ N/A _ 4. Was a label containing the same information written on the sample tube as well as the project name, number, the date, and sampler's initials taped to the outside of the core?

Yes _ No _ N/A _ 5. Were cores logged and stored in a cooler with commercially available Blue Ice prior to and during transport to the support facility sampling area where they were logged for shipment?

FIELD CHECKLIST

DOCUMENT CONTROL

Yes _ No _ N/A _

1. Have all unused and voided accountable documents been returned to the coordinator by the team members?

Yes _ No _ N/A _

2. Were any accountable documents lost or destroyed? If yes, have document numbers of all lost or destroyed accountable documents been recorded and where are they recorded?

Yes _ No _ N/A _

3. Are all samples identified with sample tags? If no, how are samples identified?

Yes _ No _ N/A _

4. Are all sample tags completed (e.g., station number, location, date, time, analyses, signatures of samplers, type, preservatives, etc.)? If yes, describe types of information recorded.

Yes _ No _ N/A _

5. Are all samples collected listed on a chain-of-custody record? If yes, describe the type of chain-of-custody record used and what information is recorded.

Yes _ No _ N/A _

6. If used, are the sample tag numbers recorded on the chain-of-custody documents?

Yes _ No _ N/A _ 14. If used, are spiked samples identified?

Yes _ No _ N/A _ 15. Are logbooks signed by the individual who checked out the logbook from the project coordinator?

Yes _ No _ N/A _ 16. Are logbooks dated upon receipt from the project coordinator?

Yes _ No _ N/A _ 17. Are logbooks project-specific (by logbook or by page)?

Yes _ No _ N/A _ 18. Are logbook entries dated and identified by author?

Yes _ No _ N/A _ 19. Is the facility's approval or disapproval to take photographs noted in a logbook?

Yes _ No _ N/A _ 20. Are photographs documented in logbooks (e.g., time, date, description of subject, photographer, etc.)?

FIELD CHECKLIST

DEBRIEFING WITH PROJECT COORDINATOR

Yes _ No _ N/A _ 1. Was a debriefing held with project coordinator and/or other participants?

_____
_____
_____

Yes _ No _ N/A _ 2. Were any recommendations made to the project participants during the debriefing? If yes, list recommendations.

_____
_____
_____

Yes _ No _ N/A _ 3. Was a copy of the field checklist left with the project coordinator at the conclusion of the debriefing?

_____
_____
_____

CONTROL CHART CHECKLIST
(ONE WITH EACH WEEKLY SUBMISSION)

Contract/Task Number_____ Installation _____

1. The following items are included in this weekly control chart package covering method(s) ___
_____

2. ___ Summary

3. ___ $\bar{x}$ - R Control Charts for duplicate, high concentration spiked QA samples, and Outlier Tests.

4. ___ $\bar{x}$ - R Three-Point Moving Average Control Charts for low concentration spiked QA samples (Class 1), surrogate spiked standard matrix samples (Class 1A), Class 1B, extended range certifications (Class 1, Class 1A, and Class 1B), and Outlier Tests.

5. ___ Observations on each chart (when applicable).

   a. ___ Trend analysis.

   b. ___ Out-of-control analysis.

   c. ___ Actions taken.

   d. ___ Demonstration of resumption of control.

6. ___ Recommendations.

_____ _____
Contractor QAC Date

CERTIFICATION PERFORMANCE DATA PACKAGE CHECKLIST
(ONE FOR EACH METHOD)

Contract/Task Number _____ Installation _____

The following items are included in this Certification Performance Data Package for _____ (Analyte(s)) in _____ (Matrix).

____ Method written up in USATHAMA format.

Calibration:

____ Calibration curves from days of certification (plot of raw data).

____ Daily calibration calculations.

____ Documentation for Lack of Fit and Zero Intercept Tests.

____ Calibration check standard results.

Certification:

____ Data summary - target versus found.

____ Reporting limit, precision, and accuracy calculations.

____ Reporting limit plot.

____ Data summary - statistics.

____ Lack of Fit and Zero Intercept Tests.

____ Chromatograms from each day of certification analyses for the highest tested concentration and for the tested concentration closest to calculated reporting limit.

CERTIFICATION PERFORMANCE DATA PACKAGE CHECKLIST

___ Long run chromatogram for highest tested concentration.
___ Spectra for all target analytes (if applicable).

___ Identity and purity determinations for off-the-shelf reference materials.

_____ _____
Contractor QAC Date

PRECERTIFICATION PERFORMANCE DATA PACKAGE CHECKLIST
(ONE FOR EACH METHOD)

Contract/Task Number _____ Installation _____

The following items are included in this Precertification Performance Data Package for _____ (Analyte(s)) in _____ (Matrix).

____ Method written up in USATHAMA format.

Calibration:

____ Calibration data and curves (plot of raw data).

____ Documentation for Lack of Fit and Zero Intercept Tests.

____ Calibration check standard results

____ Characterization of non-SARM material

____ Chromatograms

_____ _____
Contractor QAC Date

AUDIT CHECKLIST

	YES	NO	COMMENT
PRE-AUDIT			
1. Notified laboratory			
2. Notified project officer			
3. Made travel arrangements			
4. Reviewed background information/ data			
5. Requested laboratory to have data/ methods/personnel available			
6. Prepared agenda			
IN-BRIEFING			
7. Introduced participants			
8. Described goals and objectives of audit/agenda			
9. Identified specific areas for review that could require some laboratory preparation			
10. Discussed general overview/status on project			
11. Discussed problem areas			

	YES	NO	COMMENT
GENERAL			
12. a. Has detailed Project QC Plan (QAPjP) been submitted?			
b. Has individual been appointed as QAC who is independent from analysis?			
c. Have sufficient facilities, personnel, and instrumentation been provided to perform the required analyses?			
d. Does the QAC have the resources to function effectively?			
e. Are chemicals and reagents of sufficient quality so as not to compromise the analytical system?			
f. Is housekeeping commensurate with analytical techniques?			
g. Has a training plan been developed and training been documented?			
h. Is the correct version of USATHAMA supplied software being used?			

AUDIT	YES	NO	COMMENT
13. Samples chosen to follow through laboratory:			
Inorganic			
Organic			
14. Sample receiving:			
a. Are procedures/SOPs available?			
b. Are samples checked upon receipt?			
c. Is the sample checking documented?			
d. Is area secure?			
e. Are chain-of-custody forms filed?			
f. Are internal chain-of-custody forms generated?			
g. Are samples logged in according to SOP?			
h. Are USATHAMA numbers assigned?			
i. Are numbers allocated for QC samples?			

AUDIT (cont)	YES	NO	COMMENT
j. Are samples stored in refrigerator until needed?			
k. Is the temperature of refrigerator monitored?			
l. Is there a sign-out system for samples?			
m. Are VOA samples isolated from other samples?			
15. Inorganics Section:			
a. Are logbooks kept for:			
Digestion?			
Analysis?			
Instrument maintenance?			
Standard preparation?			
b. Are logbooks identified with unique number?			
c. Are pages of logbooks numbered?			
d. Are reagents/solvents/acids checked for purity, etc.?			

Inorganics (cont)	YES	NO	COMMENT
e. Are standards stored correctly?			
f. Is inventory of standards maintained?			
g. Are standard solutions labelled with date prepared?			
h. Are solution validity checks documented?			
i. Are standards traceable from receipt to use?			
j. Are samples maintained and stored according to SOP?			
k. Are procedures in place to minimize cross contamination?			
l. Are samples analyzed according to certified methods?			
m. Are results of analyses stored in data packages?			
16. Organics Section:			
a. Are logbooks kept for:			
Extraction?			
Analysis?			

Organics Section (cont)	YES	NO	COMMENT
Instrument Maintenance?			
Standard preparation?			
b. Are logbooks identified with unique number?			
c. Are pages in logbooks numbered?			
d. Are reagents/chemicals checked for purity, etc.?			
e. Are standards stored correctly?			
f. Is an inventory of standards maintained?			
g. Are standard solutions labelled with date prepared?			
h. Are solution validity checks documented?			
i. Are standards traceable from receipt to use?			
j. Are samples maintained and stored according to SOP?			
k. Are procedures in place to minimize cross contamination?			

Organics (cont)	YES	NO	COMMENT
l. Is tuning of GC/MS performed and documented every 12 hours?			
m. Are samples analyzed according to certified methods?			
n. Are results of analyses stored in data packages?			
17. Method selected is performed according to written certified method?			
18. Have problem areas been discussed and corrective actions reviewed/ recommended?			
19. Data Management:			
a. Data packages prepared for each lot of analysis?			
b. Data packages readily available for review?			
c. Representative data packages from each method reviewed?			
d. Data package checklists included in each package?			
Filled out correctly?			
e. Notebook pages signed and dated?			

Data Management (cont)	YES	NO	COMMENT
f. Computer print-outs readily identified?			
g. Data processing according to SOPs?			
h. Data transmittal to USATHAMA according to SOPs?			
20. Has data been validated according to USATHAMA internal SOP?			
OUTBRIEFING			
21. Summary given on findings, observations, conclusions reached?			
22. Responded to laboratory questions/ concerns?			
23. Provided forum to rectify differences between laboratory staff and audit team?			
24. Identified deficiencies and offered assistance in their correction?			
25. Copy of completed audit checklist provided to laboratory?			
26. Discussed future goals and objectives?			

Appendix C: Non-USAEC Methods

METHOD 8080

ORGANOCHLORINE PESTICIDES AND PCBs

1.0 SCOPE AND APPLICATION

1.1 Method 8080 is used to determine the concentration of various organochlorine pesticides and polychlorinated biphenyls (PCBs). Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

2.0 SUMMARY OF METHOD

2.1 Method 8080 provides gas chromatographic conditions for the detection of ppb levels of certain organochlorine pesticides and PCBs. Prior to the use of this method, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL sample is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or a halogen-specific detector (HSD).

2.2 The sensitivity of Method 8080 usually depends on the level of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, Method 8080 may also be performed on samples that have undergone cleanup. Method 3620, Florisil Column Cleanup, by itself or followed by Method 3660, Sulfur Cleanup, may be used to eliminate interferences in the analysis.

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Section 3.5, in particular), 3600, and 8000.

3.2 Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large late-eluting peaks, especially in the 15% and 50% fractions from the Florisil cleanup. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination. The contamination from phthalate esters can be completely eliminated with a microcoulometric or electrolytic conductivity detector.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

5.0 REAGENTS

5.1 Solvents: Hexane, acetone, toluene, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions at a concentration of 1.00 ug/uL by dissolving 0.0100 g of assayed reference material in isooctane and diluting to volume in a 10-mL volumetric flask. A small volume of toluene may be necessary to put some pesticides in solution. Larger volumes can be used at the convenience of the analyst. When compound purity is assayed to be 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standards should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest are prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

5.4 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.4.1 Prepare calibration standards at a minimum of five concentration levels for each analyte of interest as described in Paragraph 5.3.

5.4.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with isooctane.

5.4.3 Analyze each calibration standard according to Section 7.0.

7.1.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C, if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis if further cleanup is not required.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Column temperature is set at 200°C isothermal. When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 160°C.

7.2.2 **Column 2:** Set 5% methane/95% argon carrier gas flow at 60 mL/min flow rate. Column temperature held isothermal at 200°C. When analyzing for the low molecular weight PCBs (PCB 1221-PCB 1248), it is advisable to set the oven temperature to 140°C.

7.2.3 When analyzing for most or all of the analytes in this method, adjust the oven temperature and column gas flow so that 4,4'-DDT has a retention time of approximately 12 min.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.3.2 Because of the low concentration of pesticide standards injected on a GC/ECD, column adsorption may be a problem when the GC has not been used for a day. Therefore, the GC column should be primed or deactivated by injecting a PCB or pesticide standard mixture approximately 20 times more concentrated than the mid-level standard. Inject this prior to beginning initial or daily calibration.

7.4 Gas chromatographic analysis:

7.4.1 Refer to Method 8000. If the internal standard calibration technique is used, add 10 uL of internal standard to the sample prior to injection.

7.4.2 Follow Section 7.6 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, and identification criteria. Include a mid-level standard after each group of 10 samples in the analysis sequence.

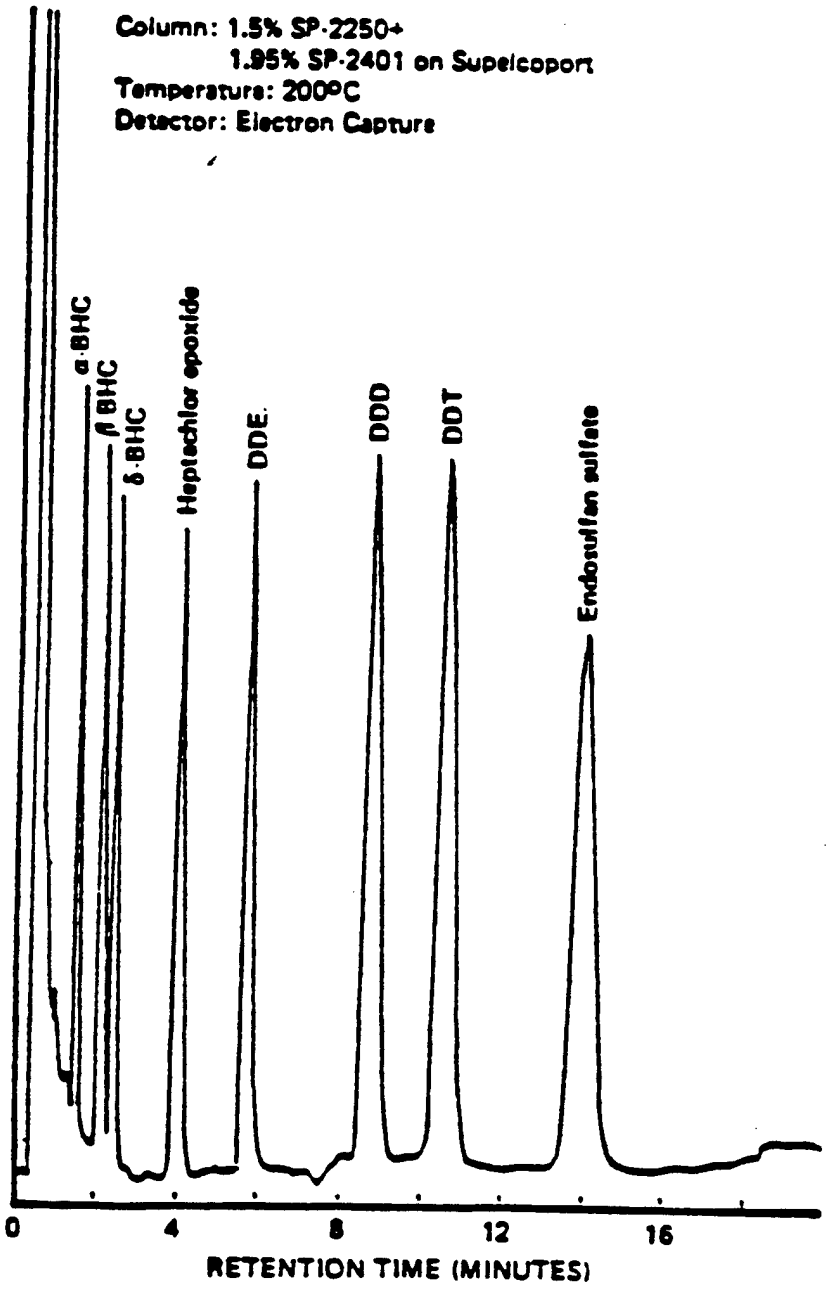


Figure 1. Gas chromatogram of pesticides.

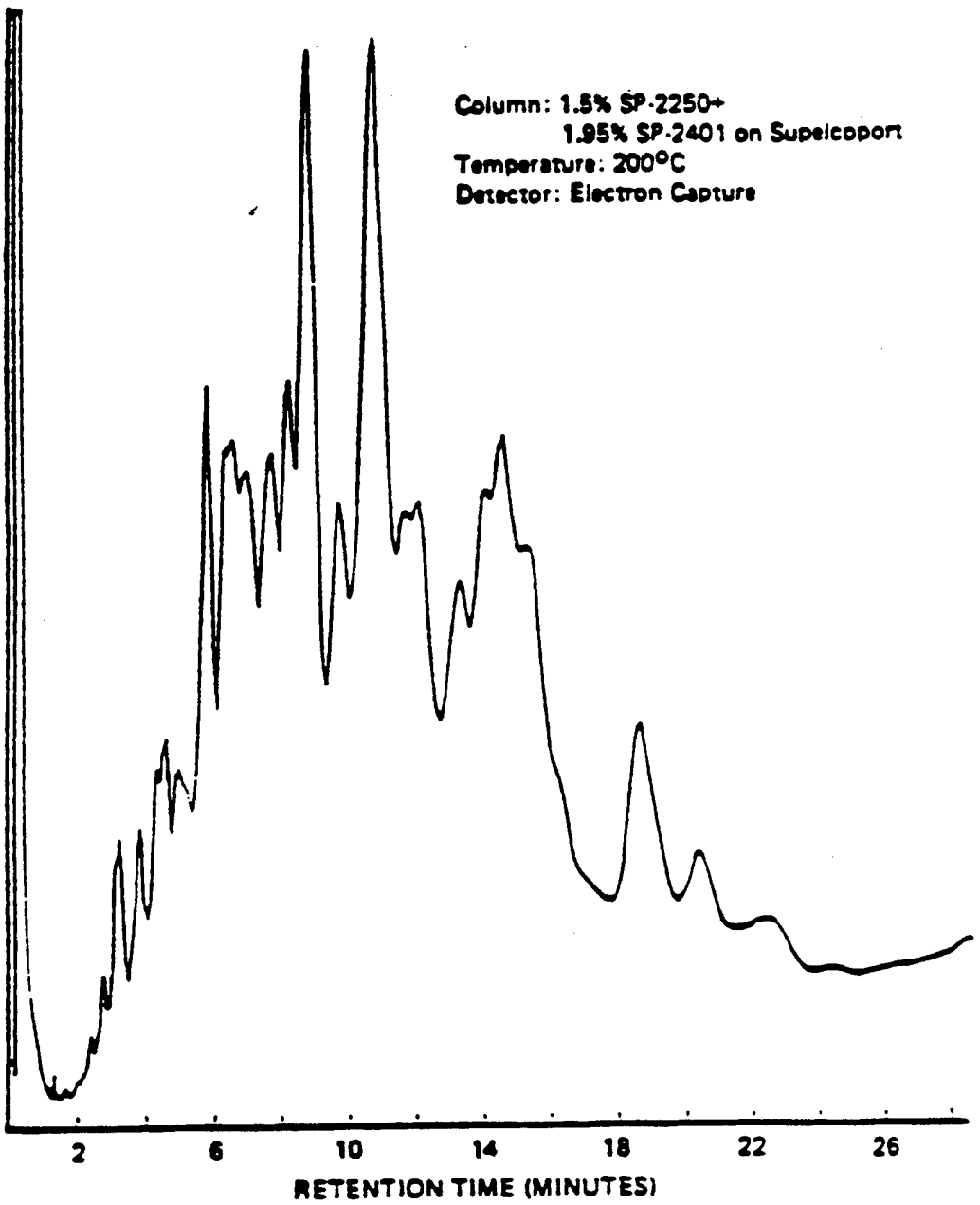


Figure 3. Gas chromatogram of toxaphene.

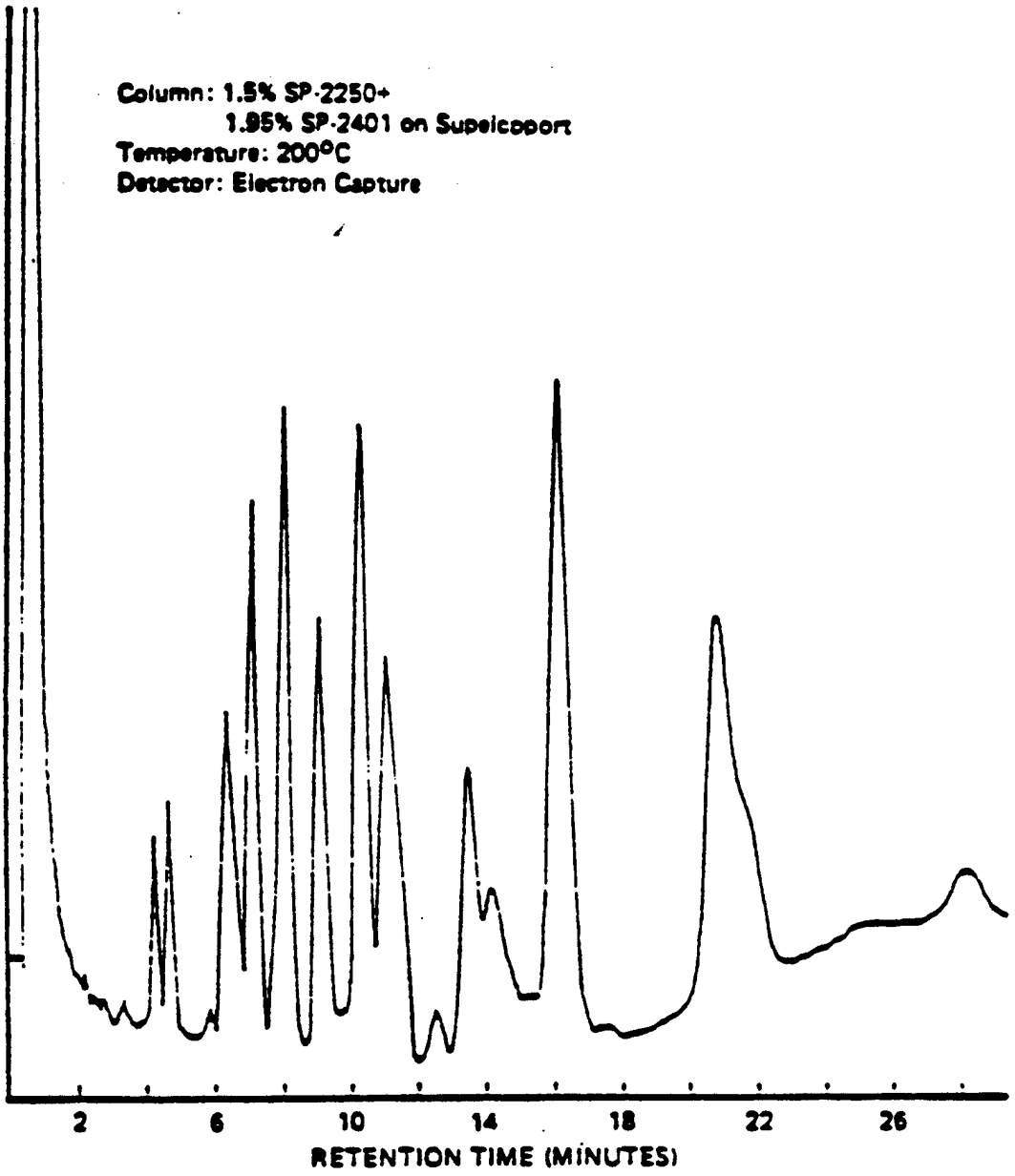


Figure 5. Gas chromatogram of PCB-1260.

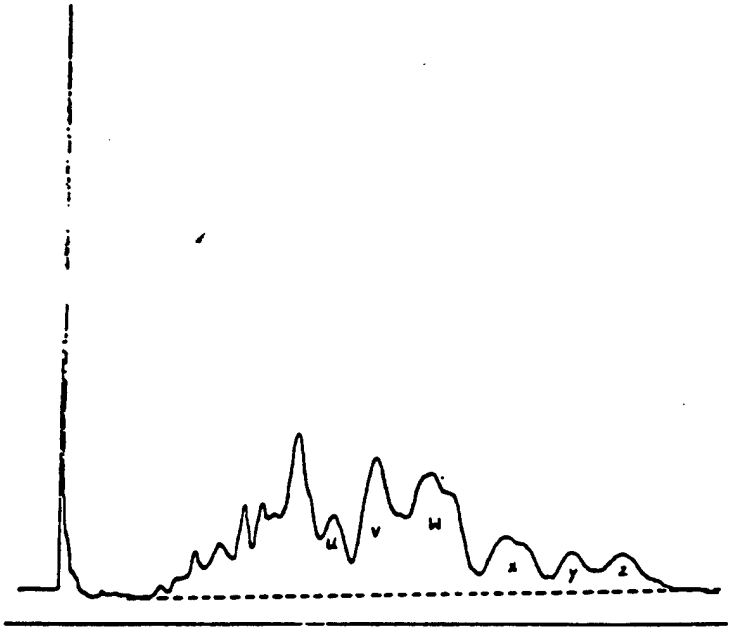


Fig. 7a--Baseline construction for multiple residues with standard toxaphene.

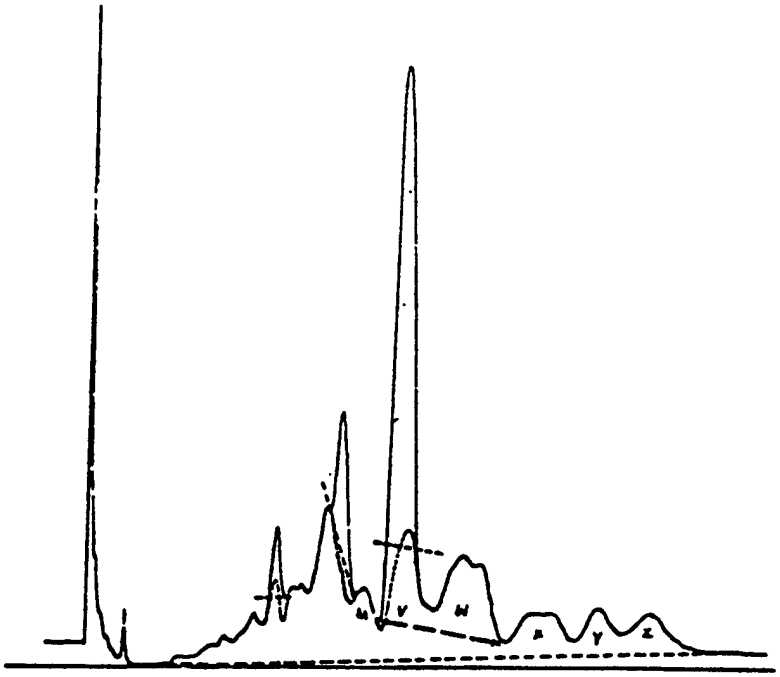


Fig. 7b--Baseline construction for multiple residues with toxaphene, DDE and o,p'-, and p,p'-DDT.

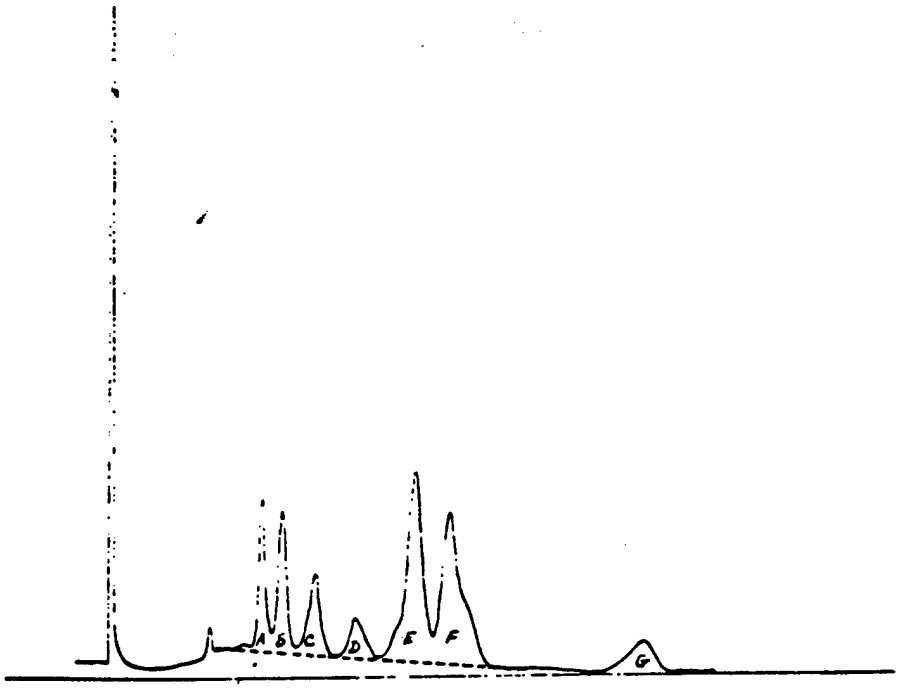


Fig. 9a--Baseline construction for multiple residues: standard chlordane.

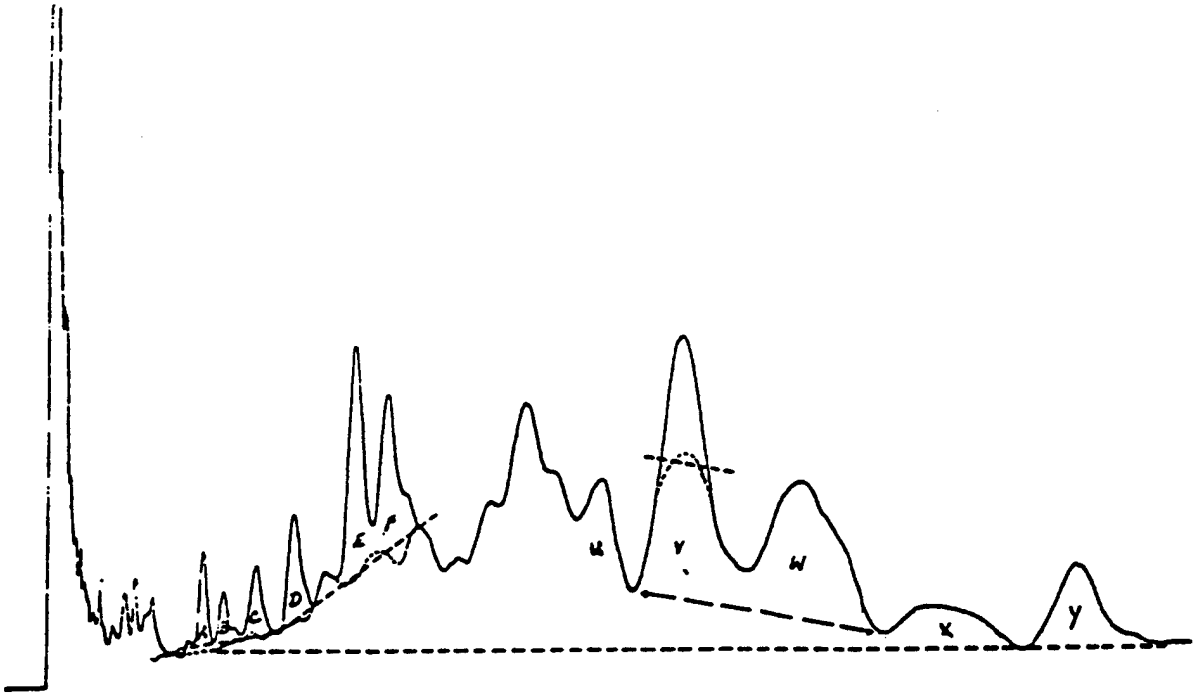


Fig. 9b--Baseline construction for multiple residues: rice bran with chlordane, toxaphene, and DDT.

D, a chlordane analog; G, coelution of cis-nonachlor and "Compound K," a chlordane isomer. The right "shoulder" of peak F is caused by trans-nonachlor.

7.6.4.1 The GC pattern of a chlordane residue may differ considerably from that of the technical standard. Depending on the sample substrate and its history, residues of chlordane can consist of almost any combination of: constituents from the technical chlordane; plant and/or animal metabolities; and products of degradation caused by exposure to environmental factors such as water and sunlight. Only limited information is available on which residue GC patterns are likely to occur in which samples types, and even this information may not be applicable to a situation where the route of exposure is unusual. For example, fish exposed to a recent spill of technical chlordane will contain a residue drastically different from a fish whose chlordane residue was accumulated by ingestion of smaller fish or of vegetation, which in turn had accumulated residues because chlordane was in the water from agricultural runoff.

7.6.4.2 Because of this inability to predict a chlordane residue GC pattern, it is not possible to prescribe a single method for the quantitation of chlordane residues. The analyst must judge whether or not the residue's GC pattern is sufficiently similar to that of a technical chlordane reference material to use the latter as a reference standard for quantitation.

7.6.4.3 When the chlordane residue does not resemble technical chlordane, but instead consists primarily of individual, identifiable peaks, quantitate each peak separately against the appropriate reference materials and report the individual residues. (Reference materials are available for at least 11 chlordane constituents, metabolites or degradation products which may occur in the residue.)

7.6.4.4 When the GC pattern of the residue resembles that of technical chlordane, quantitate chlordane residues by comparing the total area of the chlordane chromatogram from peaks A through F (Figure 9a) in the sample versus the same part of the standard chromatogram. Peak G may be obscured in a sample by the presence of other pesticides. If G is not obscured, include it in the measurement for both standard and sample. If the heptachlor epoxide peak is relatively small, include it as part of the total chlordane area for calculation of the residue. If heptachlor and/or heptachlor epoxide are much out of proportion as in Figure 6j, calculate these separately and subtract their areas from total area to give a corrected chlordane area. (Note that octachlor epoxide, metabolite of chlordane, can easily be mistaken for heptachlor epoxide on a nonpolar GC column.)

7.6.5.3 Quantitate PCB residues by comparing total area or height of residue peaks to total area of height of peaks from appropriate Aroclor(s) reference materials. Measure total area or height response from common baseline under all peaks. Use only those peaks from sample that can be attributed to chlorobiphenyls. These peaks must also be present in chromatogram of reference materials. Mixture of Aroclors may be required to provide best match of GC patterns of sample and reference.

7.6.6 **DDT:** DDT found in samples often consists of both o,p'- and p,p'-DDT. Residues of DDE and TDE are also frequently present. Each isomer of DDT and its metabolites should be quantitated using the pure standard of that compound and reported as such.

7.6.7 **Hexachlorocyclohexane (BHC, from the former name, benzene hexachloride):** Technical grade BHC is a cream-colored amorphous solid with a very characteristic musty odor; it consists of a mixture of six chemically distinct isomers and one or more heptachloro-cyclohexanes and octachloro-cyclohexanes.

7.6.7.1 Commercial BHC preparations may show a wide variance in the percentage of individual isomers present. The elimination rate of the isomers fed to rats was 3 weeks for the α-, γ-, and δ-isomers and 14 weeks for the β-isomer. Thus it may be possible to have any combination of the various isomers in different food commodities. BHC found in dairy products usually has a large percentage of β-isomer.

7.6.7.2 Individual isomers (α, β, γ, and δ) were injected into gas chromatographs equipped with flame ionization, microcoulometric, and electron capture detectors. Response for the four isomers is very nearly the same whether flame ionization or microcoulometric GLC is used. The α-, γ-, and δ-isomers show equal electron affinity. β-BHC shows a much weaker electron affinity compared to the others isomers.

7.6.7.3 Quantitate each isomer (α, β, γ, and δ) separately against a standard of the respective pure isomer, using a GC column which separates all the isomers from one another.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures. Quality control to validate sample extraction is covered in Method 3500 and in the extraction method utilized. If extract cleanup was performed, follow the QC in Method 3600 and in the specific cleanup method.

8.2 Mandatory quality control to evaluate the GC system operation is found in Method 8000, Section 8.6.

9.0 METHOD PERFORMANCE

9.1 The method was tested by 20 laboratories using reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations. Concentrations used in the study ranged from 0.5 to 30 ug/L for single-component pesticides and from 8.5 to 400 ug/L for multi-component parameters. Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix. Linear equations to describe these relationships for a flame ionization detector are presented in Table 4.

9.2 The accuracy and precision obtained will be determined by the sample matrix, sample-preparation technique, optional cleanup techniques, and calibration procedures used.

10.0 REFERENCES

1. U.S. EPA, "Development and Application of Test Procedures for Specific Organic Toxic Substances in Wastewaters, Category 10: Pesticides and PCBs," Report for EPA Contract 68-03-2605.

2. U.S. EPA, "Interim Methods for the Sampling and Analysis of Priority Pollutants in Sediments and Fish Tissue," Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, October 1980.

3. Pressley, T.A., and J.E. Longbottom, "The Determination of Organohalide Pesticides and PCBs in Industrial and Municipal Wastewater: Method 617," U.S. EPA/EMSL, Cincinnati, OH, EPA-600/4-84-006, 1982.

4. "Determination of Pesticides and PCB's in Industrial and Municipal Wastewaters, U.S. Environmental Protection Agency," Environmental Monitoring and Support Laboratory, Cincinnati, OH 45268, EPA-600/4-82-023, June 1982.

5. Goerlitz, D.F. and L.M. Law, Bulletin for Environmental Contamination and Toxicology, 6, 9, 1971.

6. Burke, J.A., "Gas Chromatography for Pesticide Residue Analysis; Some Practical Aspects," Journal of the Association of Official Analytical Chemists, 48, 1037, 1965.

7. Webb, R.G. and A.C. McCall, "Quantitative PCB Standards for Electron Capture Gas Chromatography," Journal of Chromatographic Science, 11, 366, 1973.

8. Millar, J.D., R.E. Thomas and H.J. Schattenberg, "EPA Method Study 18, Method 608: Organochlorine Pesticides and PCBs," U.S. EPA/EMSL, Research Triangle Park, NC, EPA-600/4-84-061, 1984.

9. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

TABLE 3. QC ACCEPTANCE CRITERIA[a]

Parameter	Test conc. (ug/L)	Limit for s (ug/L)	Range for $\bar{X}$ (ug/L)	Range P, P_S (%)
Aldrin	2.0	0.42	1.08-2.24	42-122
α-BHC	2.0	0.48	.98-2.44	37-134
β-BHC	2.0	0.64	0.78-2.60	17-147
δ-BHC	2.0	0.72	1.01-2.37	19-140
γ-BHC	2.0	0.46	0.86-2.32	32-127
Chlordane	50	10.0	27.6-54.3	45-119
4,4'-DDD	10	2.8	4.8-12.6	31-141
4,4'-DDE	2.0	0.55	1.08-2.60	30-145
4,4'-DDT	10	3.6	4.6-13.7	25-160
Dieldrin	2.0	0.76	1.15-2.49	36-146
Endosulfan I	2.0	0.49	1.14-2.82	45-153
Endosulfan II	10	6.1	2.2-17.1	D-202
Endosulfan Sulfate	10	2.7	3.8-13.2	26-144
Endrin	10	3.7	5.1-12.6	30-147
Heptachlor	2.0	0.40	0.86-2.00	34-111
Heptachlor epoxide	2.0	0.41	1.13-2.63	37-142
Toxaphene	50	12.7	27.8-55.6	41-126
PCB-1016	50	10.0	30.5-51.5	50-114
PCB-1221	50	24.4	22.1-75.2	15-178
PCB-1232	50	17.9	14.0-98.5	10-215
PCB-1242	50	12.2	24.8-69.6	39-150
PCB-1248	50	15.9	29.0-70.2	38-158
PCB-1254	50	13.8	22.2-57.9	29-131
PCB-1260	50	10.4	18.7-54.9	8-127

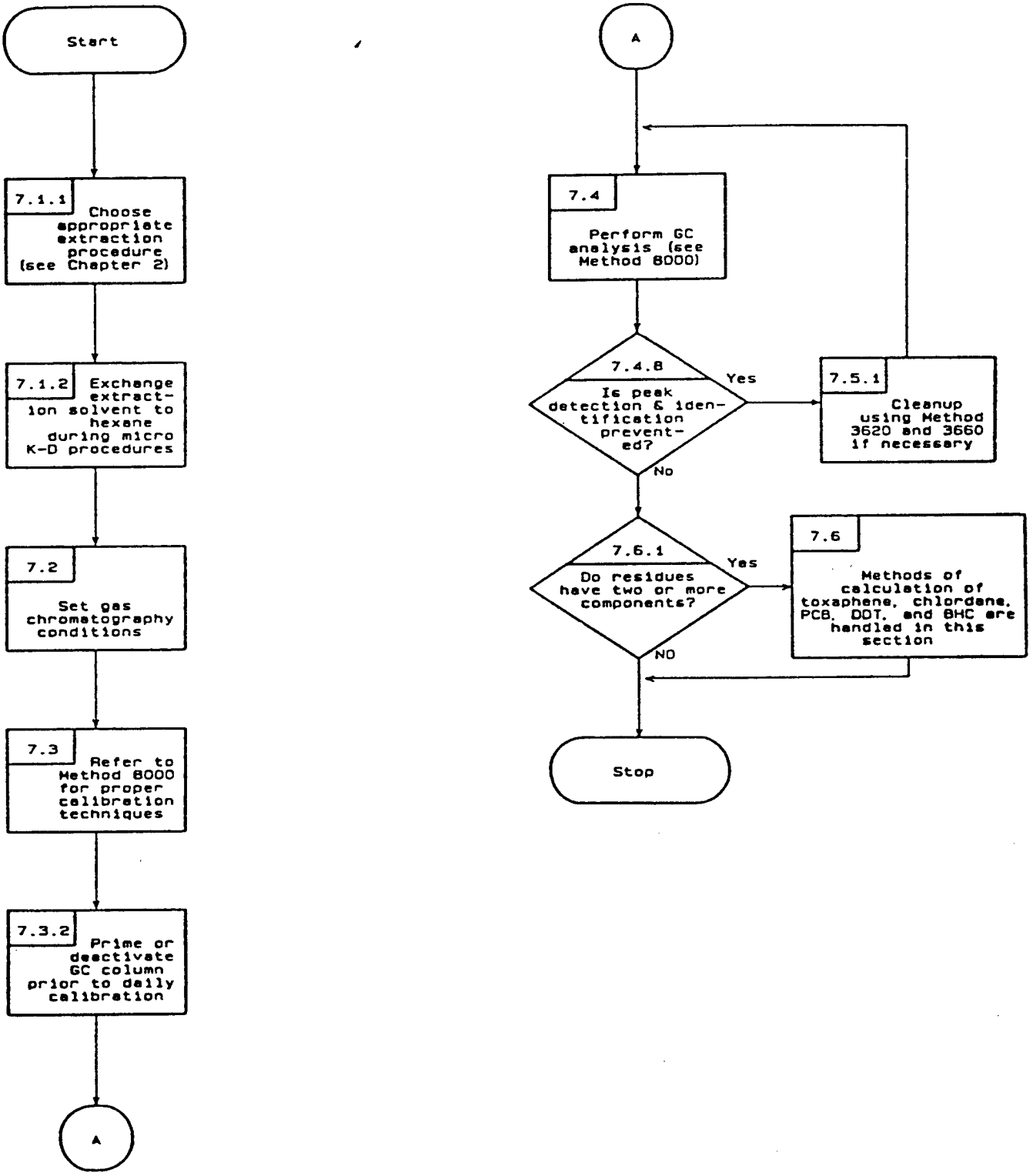
s = Standard deviation of four recovery measurements, in ug/L.

$\bar{X}$ = Average recovery for four recovery measurements, in ug/L.

P, P_S = Percent recovery measured.

D = Detected; result must be greater than zero.

[a]Criteria from 40 CFR Part 136 for Method 608. These criteria are based directly upon the method performance data in Table 4. Where necessary, the limits for recovery have been broadened to assure applicability of the limits to concentrations below those used to develop Table 4.


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2)
7.1.2 Exchange extraction solvent to hexane during micro K-D procedures
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
7.3.2 Prime or deactivate GC column prior to daily calibration
A
A
7.4 Perform GC analysis (see Method 8000)
7.4.8 Is peak detection & identification prevented?
Yes
7.5.1 Cleanup using Method 3620 and 3660 if necessary
No
7.6.1 Do residues have two or more components?
Yes
7.6 Methods of calculation of toxaphene, chlordane, PCB, DDT, and BHC are handled in this section
NO
Stop

METHOD 8140

ORGANOPHOSPHORUS PESTICIDES

1.0 SCOPE AND APPLICATION

1.1 Method 8140 is a gas chromatographic (GC) method used to determine the concentration of various organosphosphorus pesticides. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

1.2 When Method 8140 is used to analyze unfamiliar samples, compound identifications should be supported by at least two additional qualitative techniques if mass spectroscopy is not employed. Section 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

2.0 SUMMARY OF METHOD

2.1 Method 8140 provides gas chromatographic conditions for the detection of ppb levels of organophosphorus pesticides. Prior to analysis, appropriate sample extraction techniques must be used. Both neat and diluted organic liquids (Method 3580, Waste Dilution) may be analyzed by direct injection. A 2- to 5-uL aliquot of the extract is injected into a gas chromatograph, and compounds in the GC effluent are detected with a flame photometric or thermionic detector.

2.2 If interferences are encountered in the analysis, Method 8140 may also be performed on extracts that have undergone cleanup using Method 3620 and/or Method 3660.

3.0 INTERFERENCES

3.1 Refer to Methods 3500 (Section 3.5, in particular), 3600, and 8000.

3.2 The use of Florisil cleanup materials (Method 3620) for some of the compounds in this method has been demonstrated to yield recoveries less than 85% and is therefore not recommended for all compounds. Refer to Table 2 of Method 3620 for recoveries of organophosphorous pesticides as a function of Florisil fractions. Use of phosphorus- or halogen-specific detectors, however, often obviates the necessity for cleanup for relatively clean sample matrices. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each analyte is no less than 85%.

TABLE 2. DETERMINATION OF PRACTICAL QUANTITATION LIMITS (PQL) FOR VARIOUS MATRICES[a]

Matrix	Factor[b]
Ground water	10
Low-level soil by sonication with GPC cleanup	670
High-level soil and sludges by sonication	10,000
Non-water miscible waste	100,000

[a]Sample PQLs are highly matrix-dependent. The PQLs listed herein are provided for guidance and may not always be achievable.

[b]PQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

4.4.2 Evaporation flask: 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.4.3 Snyder column: Three-ball macro (Kontes K-503000-0121 or equivalent).

4.4.4 Snyder column: Two-ball micro (Kontes K-569001-0219 or equivalent).

4.5 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.6 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.7 Microsyringe: 10-uL.

4.8 Syringe: 5-mL.

4.9 Volumetric flasks: 10-, 50-, and 100-mL, ground-glass stopper.

5.0 REAGENTS

5.1 Solvents: Hexane, acetone, isooctane (2,2,4-trimethylpentane) (pesticide quality or equivalent).

5.2 Stock standard solutions:

5.2.1 Prepare stock standard solutions by accurately weighing about 0.0100 g of pure material. Dissolve the material in hexane or other suitable solvent and dilute to volume in a 10-mL volumetric flask. Larger volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.2.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.2.3 Stock standard solutions must be replaced after one year, or sooner if comparison with check standards indicates a problem.

5.3 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest should be prepared through dilution of the stock standards with isooctane. One of the concentration levels should be at a concentration near, but above, the method detection

7.1.2.1 Following K-D of the methylene chloride extract to 1 mL using the macro-Snyder column, allow the apparatus to cool and drain for at least 10 min.

7.1.2.2 Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the macro-Snyder column. Concentrate the extract using 1 mL of hexane to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration in 5-10 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

7.1.2.3 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane. A 5-mL syringe is recommended for this operation. Adjust the extract volume to 10.0 mL. Stopper the concentrator tube and store refrigerated at 4°C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a Teflon-sealed screw-cap vial. Proceed with gas chromatographic analysis if further cleanup is not required.

7.2 Gas chromatography conditions (Recommended):

7.2.1 **Column 1a:** Set helium carrier gas flow at 30 mL/min flow rate. Column temperature is set at 150°C for 1 min and then programmed at 25°C/min to 220°C and held.

7.2.2 **Column 1b:** Set nitrogen carrier gas flow at 30 mL/min flow rate. Column temperature is set at 170°C for 2 min and then programmed at 20°C/min to 220°C and held.

7.2.3 **Column 2:** Set helium carrier gas at 25 mL/min flow rate. Column temperature is set at 170°C for 7 min and then programmed at 10°C/min to 250°C and held.

7.2.4 **Column 3:** Set nitrogen carrier gas at 30 mL/min flow rate. Column temperature is set at 100°C and then immediately programmed at 25°C/min to 200°C and held.

7.3 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

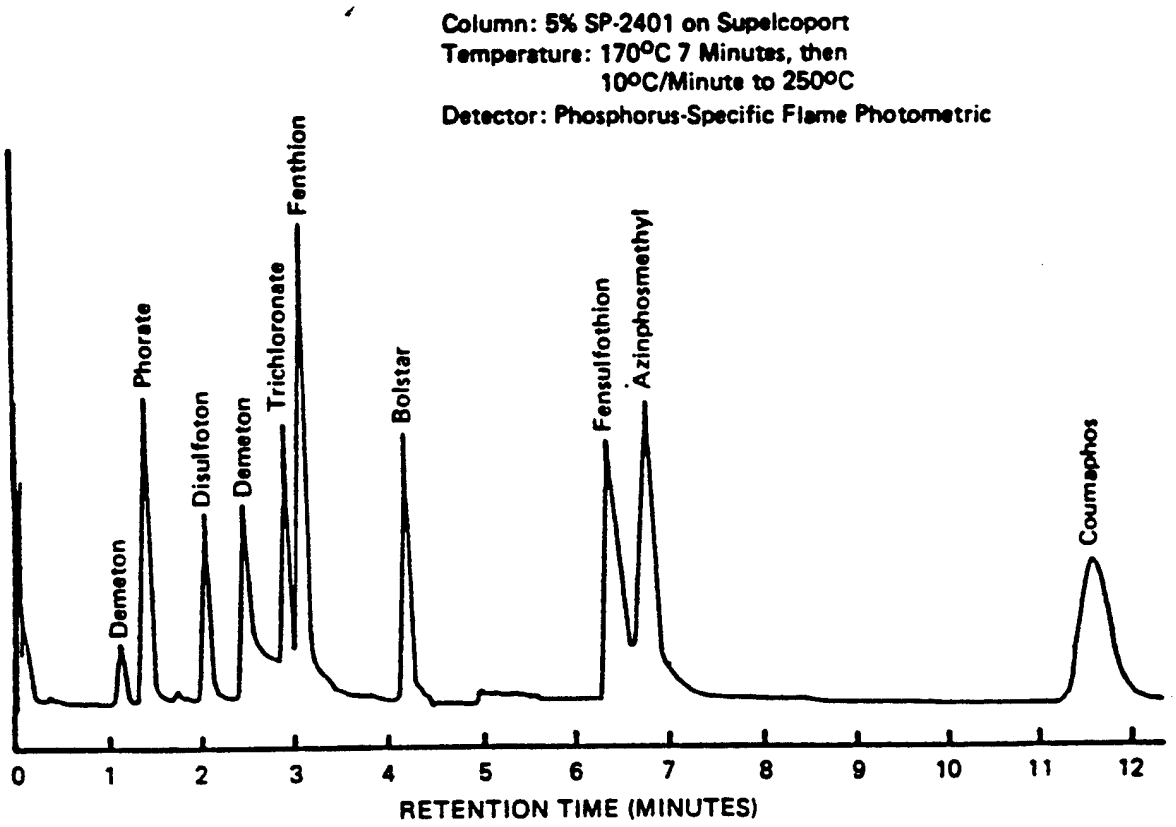


Figure 1. Gas chromatogram of organophosphorus pesticides (Example 1).

Column: 15% SE–54 on Gas Chrom Q
Temperature: 100°C Initial, then
25°C/Minute to 200°C
Detector: Hall Electrolytic Conductivity–Oxidative Mode

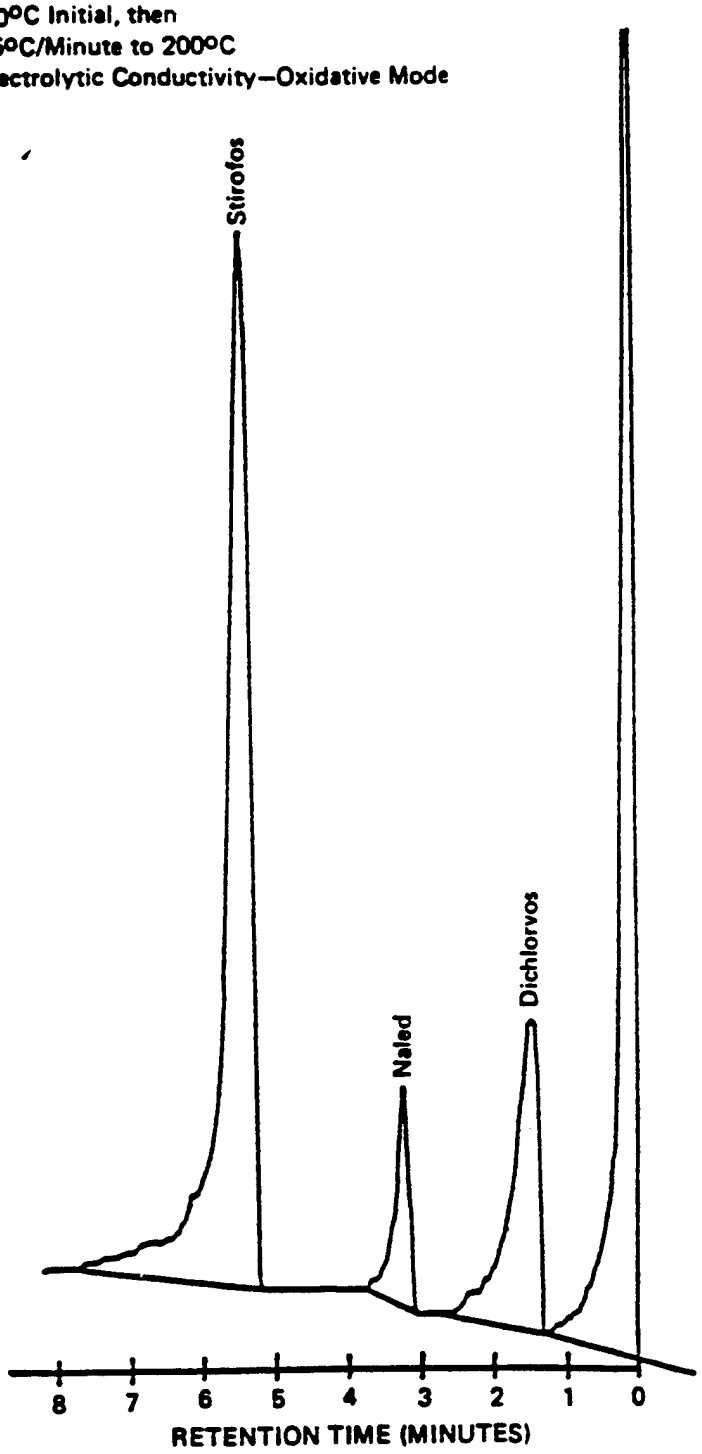


Figure 3. Gas chromatogram of organophosphorus pesticides (Example 3).

8.2.1 Select a representative spike concentration for each analyte to be measured. The quality control check sample concentrate (Method 8000, Section 8.6) should contain each analyte in acetone at a concentration 1,000 times more concentrated than the selected spike concentration.

8.2.2 Table 3 indicates Single Operator Accuracy and Precision for this method. Compare the results obtained with the results given in Table 3 to determine if the data quality is acceptable.

8.3 Calculate surrogate standard recovery on all samples, blanks, and spikes. Determine if the recovery is within limits (limits established by performing QC procedures outlined in Method 8000, Section 8.10).

8.3.1 If recovery is not within limits, the following procedures are required.

- Check to be sure there are no errors in calculations, surrogate solutions and internal standards. Also, check instrument performance.
- Recalculate the data and/or reanalyze the extract if any of the above checks reveal a problem.
- Reextract and reanalyze the sample if none of the above are a problem or flag the data as "estimated concentration."

8.4 GC/MS confirmation:

8.4.1 GC/MS techniques should be judiciously employed to support qualitative identifications made with this method. The GC/MS operating conditions and procedures for analysis are those specified in Method 8270.

8.4.2 When available, chemical ionization mass spectra may be employed to aid in the qualitative identification process.

8.4.3 Should these MS procedures fail to provide satisfactory results, additional steps may be taken before reanalysis. These steps may include the use of alternate packed or capillary GC columns and additional cleanup.

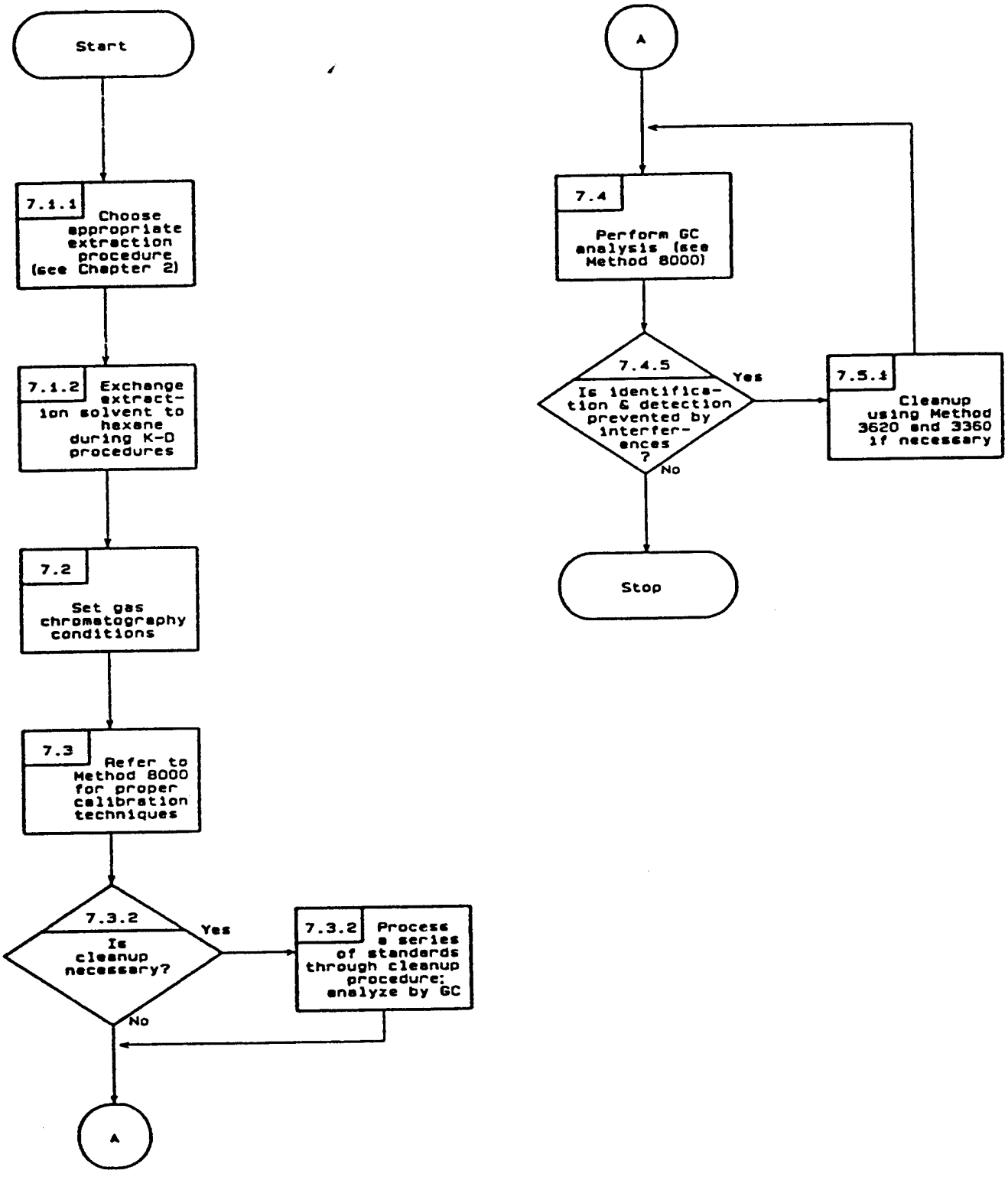
9.0 METHOD PERFORMANCE

9.1 Single-operator accuracy and precision studies have been conducted using spiked wastewater samples. The results of these studies are presented in Table 3.

TABLE 3. SINGLE-OPERATOR ACCURACY AND PRECISION[a]

Parameter	Average recovery (%)	Standard deviation (%)	Spike range (ug/L)	Number of analyses
Azinphos methyl	72.7	18.8	21-250	17
Bolstar	64.6	6.3	4.9-46	17
Chlorpyrifos	98.3	5.5	1.0-50.5	18
Coumaphos	109.0	12.7	25-225	17
Demeton	67.4	10.5	11.9-314	17
Diazinon	67.0	6.0	5.6	7
Dichlorvos	72.1	7.7	15.6-517	16
Disulfoton	81.9	9.0	5.2-92	17
Ethoprop	100.5	4.1	1.0-51.5	18
Fensulfothion	94.1	17.1	23.9-110	17
Fenthion	68.7	19.9	5.3-64	17
Merphos	120.7	7.9	1.0-50	18
Mevinphos	56.5	7.8	15.5-520	16
Naled	78.0	8.1	25.8-294	16
Parathion methyl	96.0	5.3	0.5-500	21
Phorate	62.7	8.9	4.9-47	17
Ronnel	99.2	5.6	1.0-50	18
Stirophos	66.1	5.9	30.3-505	16
Tokuthion	64.6	6.8	5.3-64	17
Trichloronate	105.0	18.6	20	3

[a]Information taken from Reference 4.


Start
7.1.1 Choose appropriate extraction procedure (see Chapter 2)
7.1.2 Exchange extraction solvent to hexane during K-D procedures
7.2 Set gas chromatography conditions
7.3 Refer to Method 8000 for proper calibration techniques
7.3.2 Is cleanup necessary?
Yes
7.3.2 Process a series of standards through cleanup procedure; analyze by GC
No
A
A
7.4 Perform GC analysis (see Method 8000)
7.4.5 Is identification & detection prevented by interferences ?
Yes
7.5.1 Cleanup using Method 3620 and 3360 if necessary
No
Stop

METHOD 8150

CHLORINATED HERBICIDES

1.0 SCOPE AND APPLICATION

1.1 Method 8150 is a gas chromatographic (GC) method for determining certain chlorinated acid herbicides. Table 1 indicates compounds that may be determined by this method and lists the method detection limit for each compound in reagent water. Table 2 lists the practical quantitation limit (PQL) for other matrices.

1.2 When Method 8150 is used to analyze unfamiliar samples, compound identifications should be supported by at least one additional qualitative technique. This method describes analytical conditions for a second gas chromatographic column that can be used to confirm measurements made with the primary column. Section 8.4 provides gas chromatograph/mass spectrometer (GC/MS) criteria appropriate for the qualitative confirmation of compound identifications.

1.3 Only experienced analysts should be allowed to work with diazomethane due to the potential hazards associated with its use (the compound is explosive and carcinogenic).

2.0 SUMMARY OF METHOD

2.1 Method 8150 provides extraction, esterification, and gas chromatographic conditions for the analysis of chlorinated acid herbicides. Spiked samples are used to verify the applicability of the chosen extraction technique to each new sample type. The esters are hydrolyzed with potassium hydroxide, and extraneous organic material is removed by a solvent wash. After acidification, the acids are extracted with solvent and converted to their methyl esters using diazomethane as the derivatizing agent. After excess reagent is removed, the esters are determined by gas chromatography employing an electron capture detector, microcoulometric detector, or electrolytic conductivity detector (Goerlitz and Lamar, 1967). The results are reported as the acid equivalents.

2.2 The sensitivity of Method 8150 usually depends on the level of interferences rather than on instrumental limitations.

3.0 INTERFERENCES

3.1 Refer to Method 8000.

3.2 Organic acids, especially chlorinated acids, cause the most direct interference with the determination. Phenols, including chlorophenols, may also interfere with this procedure.

3.3 Alkaline hydrolysis and subsequent extraction of the basic solution remove many chlorinated hydrocarbons and phthalate esters that might otherwise interfere with the electron capture analysis.

3.4 The herbicides, being strong organic acids, react readily with alkaline substances and may be lost during analysis. Therefore, glassware and glass wool must be acid-rinsed, and sodium sulfate must be acidified with sulfuric acid prior to use to avoid this possibility.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: Analytical system complete with gas chromatograph suitable for on-column injections and all required accessories, including detectors, column supplies, recorder, gases, and syringes. A data system for measuring peak areas and/or peak heights is recommended.

4.1.1 **Columns:**

4.1.1.1 Column 1a and 1b: 1.8-m x 4-mm I.D. glass, packed with 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 mesh) or equivalent.

4.1.1.2 Column 2: 1.8-m x 4-mm I.D. glass, packed with 5% OV-210 on Gas Chrom Q (100/120 mesh) or equivalent.

4.1.1.3 Column 3: 1.98-m x 2-mm I.D. glass, packed with 0.1% SP-1000 on 80/100 mesh Carbopack C or equivalent.

4.1.2 **Detector:** Electron capture (ECD).

4.2 Erlenmeyer flasks: 250- and 500-mL Pyrex, with 24/40 ground-glass joint.

4.3 Beaker: 500-mL.

4.4 Diazomethane generator: Refer to Section 7.3 to determine which method of diazomethane generation should be used for a particular application.

4.4.1 **Diazald kit:** recommended for the generation of diazomethane using the procedure given in Section 7.3.2 (Aldrich Chemical Co., Cat. No. 210,025-2 or equivalent).

4.4.2 Assemble from two 20 x 150-mm test tubes, two Neoprene rubber stoppers, and a source of nitrogen. Use Neoprene rubber stoppers with holes drilled in them to accommodate glass delivery tubes. The exit tube must be drawn to a point to bubble diazomethane through the sample extract. The generator assembly is shown in Figure 1. The procedure for use of this type of generator is given in Section 7.3.3.

4.5 Vials: Amber glass, 10- to 15-mL capacity with Teflon-lined screw cap.

4.6 Separatory funnel: 2-L, 125-mL, and 60-mL.

4.7 Drying column: 400-mm x 20-mm I.D. Pyrex chromatographic column with Pyrex glass wool at bottom and a Teflon stopcock.
NOTE: Fritted glass discs are difficult to decontaminate after highly contaminated extracts have been passed through. Columns without frits may be purchased. Use a small pad of Pyrex glass wool to retain the adsorbent. Prewash the glass wool pad with 50 mL of acetone followed by 50 mL of elution solvent prior to packing the column with adsorbent.

4.8 Kuderna-Danish (K-D) apparatus:

4.8.1 **Concentrator tube:** 10-mL, graduated (Kontes K-570050-1025 or equivalent). Ground-glass stopper is used to prevent evaporation of extracts

4.8.2 **Evaporation flask:** 500-mL (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs.

4.8.3 **Snyder column:** Three-ball macro (Kontes K-503000-0121 or equivalent).

4.8.4 **Snyder column:** Two-ball micro (Kontes K-569001-0219 or equivalent).

4.9 Boiling chips: Solvent extracted, approximately 10/40 mesh (silicon carbide or equivalent).

4.10 Water bath: Heated, with concentric ring cover, capable of temperature control (±5°C). The bath should be used in a hood.

4.11 Microsyringe: 10-uL.

4.12 Wrist shaker: Burrell Model 75 or equivalent.

4.13 Glass wool: Pyrex, acid washed.

4.14 Balance: Analytical, capable of accurately weighting to the nearest 0.0001 g.

4.15 Syringe: 5-mL.

4.16 Glass rod.

5.0 REAGENTS

5.1 Reagent water: Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

volumes can be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight can be used without correction to calculate the concentration of the stock standard. Commerically prepared stock standards can be used at any concentration if they are certified by the manufacturer or by an independent source.

5.10.2 Transfer the stock standard solutions into Teflon-sealed screw-cap bottles. Store at 4°C and protect from light. Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

5.10.3 Stock standard solutions must be replaced after 1 year, or sooner if comparison with check standards indicates a problem.

5.11 Calibration standards: Calibration standards at a minimum of five concentration levels for each parameter of interest should be prepared through dilution of the stock standards with diethyl ether. One of the concentration levels should be at a concentration near, but above, the method detection limit. The remaining concentration levels should correspond to the expected range of concentrations found in real samples or should define the working range of the GC. Calibration solutions must be replaced after six months, or sooner if comparison with check standards indicates a problem.

5.12 Internal standards (if internal standard calibration is used): To use this approach, the analyst must select one or more internal standards that are similar in analytical behavior to the compounds of interest. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Because of these limitations, no internal standard can be suggested that is applicable to all samples.

5.12.1 Prepare calibration standards at a minimum of five concentration levels for each parameter of interest as described in Paragraph 5.11.

5.12.2 To each calibration standard, add a known constant amount of one or more internal standards, and dilute to volume with diethyl ether.

5.12.3 Analyze each calibration standard according to Section 7.0.

5.13 Surrogate standards: The analyst should monitor the performance of the extraction, cleanup (when used), and analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent water blank with one or two herbicide surrogates (e.g., herbicides that are not expected to be present in the sample) recommended to encompass the range of the temperature program used in this method. Deuterated analogs of analytes should not be used as surrogates for gas chromatographic analysis due to coelution problems.

7.1.2.2 Remove the flask from the water bath and allow to cool. Transfer the water solution to a 125-mL separatory funnel and extract the basic solutions once with 40 mL and then twice with 20 mL of diethyl ether. Allow sufficient time for the layers to separate and discard the ether layer each time. The phenoxy acid herbicides remain soluble in the aqueous phase as potassium salts.

7.1.3 **Solvent cleanup:**

7.1.3.1 Adjust the pH to 2 by adding 5 mL cold (4°C) sulfuric acid (1:3) to the separatory funnel. Be sure to check the pH at this point. Extract the herbicides once with 40 mL and twice with 20 mL of diethyl ether. Discard the aqueous phase.

7.1.3.2 Combine ether extracts in a 125-mL Erlenmeyer flask containing 1.0 g of acidified anhydrous sodium sulfate. Stopper and allow the extract to remain in contact with the acidified sodium sulfate. If concentration and esterification are not to be performed immediately, store the sample overnight in the refrigerator.

7.1.3.3 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

7.1.3.4 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

7.1.3.5 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5-mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro-Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of ethyl ether to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 min. When the apparent volume of the liquid reaches 0.5 mL, remove the micro-K-D from the

7.2.3 **Solvent cleanup:**

7.2.3.1 Acidify the contents of the separatory funnel to pH 2 by adding 2 mL of cold (4°C) sulfuric acid (1:3). Test with pH indicator paper. Add 20 mL diethyl ether and shake vigorously for 2 min. Drain the aqueous layer into a 250-mL Erlenmeyer flask, and pour the organic layer into a 125-mL Erlenmeyer flask containing about 0.5 g of acidified sodium sulfate. Repeat the extraction twice more with 10-mL aliquots of diethyl ether, combining all solvent in the 125-mL flask. Allow the extract to remain in contact with the sodium sulfate for approximately 2 hr.

7.2.3.2 Transfer the ether extract, through a funnel plugged with acid-washed glass wool, into a 500-mL K-D flask equipped with a 10-mL concentrator tube. Use a glass rod to crush caked sodium sulfate during the transfer. Rinse the Erlenmeyer flask and column with 20-30 mL of diethyl ether to complete the quantitative transfer.

7.2.3.3 Add one or two clean boiling chips to the flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL of diethyl ether to the top. Place the apparatus on a hot water bath (60°-65°C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed in vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 15-20 min. At the proper rate of distillation, the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 min.

7.2.3.4 Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of diethyl ether. A 5-mL syringe is recommended for this operation. Add a fresh boiling chip, attach a micro-Snyder column to the concentrator tube, and prewet the column by adding 0.5 mL of ethyl ether to the top. Place the micro-K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5-10 min. When the apparent volume of the liquid reaches 0.5 mL, remove the micro-K-D from the bath and allow it to drain and cool. Remove the Snyder column and add 0.1 mL of methanol. Rinse the walls of the concentrator tube while adjusting the extract volume to 1.0 mL with diethyl ether.

7.2.3.5 Determine the original sample volume by refilling the sample bottle to the mark with water and transferring to a 1-liter graduated cylinder. Record the sample volume to the nearest 5 mL.

Apply nitrogen flow (10 mL/min) to bubble diazomethane through the extract for 10 min or until the yellow color of diazomethane persists. The amount of Diazald used is sufficient for esterification of approximately three sample extracts. An additional 0.1-0.2 g of Diazald may be added (after the initial Diazald is consumed) to extend the generation of the diazomethane. There is sufficient KOH present in the original solution to perform a maximum of approximately 20 min of total esterification.

7.3.3.2 Remove the concentrator tube and seal it with a Neoprene or Teflon stopper. Store at room temperature in a hood for 20 min.

7.3.3.3 Destroy any unreacted diazomethane by adding 0.1-0.2 g silicic acid to the concentrator tube. Allow to stand until the evolution of nitrogen gas has stopped. Adjust the sample volume to 10.0 mL with hexane. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. It is recommended that the methylated extracts be analyzed immediately to minimize the trans-esterification and other potential reactions that may occur. Analyze by gas chromatography.

7.4 Gas chromatography conditions (Recommended):

7.4.1 **Column 1a:** Set 5% methane/95% argon carrier gas flow at 70-mL/min flow rate. Column temperature is set at 185°C isothermal.

7.4.2 **Column 1b:** Set 5% methane/95% argon carrier gas flow at 70-mL/min flow rate. Column temperature is set at 140°C for 6 min and then programmed at 10°C/min to 200°C and held.

7.4.3 **Column 2:** Set 5% methane/95% argon carrier gas at 70-mL/min flow rate. Column temperature is set at 185°C isothermal.

7.4.4 **Column 3:** Set nitrogen (ultra-high purity) carrier gas at 25-mL/min flow rate. Column temperature is set at 100°C and then immediately programmed at 10°C/min to 150°C and held.

7.5 Calibration: Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.5.1 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.5.2 The following gas chromatographic columns are recommended for the compounds indicated:

Column: 1.5% SP-2250/1.95% SP-2401 on Supelcoport (100/120 Mesh)
Temperature: Isothermal at 185°C
Detector: Electron Capture

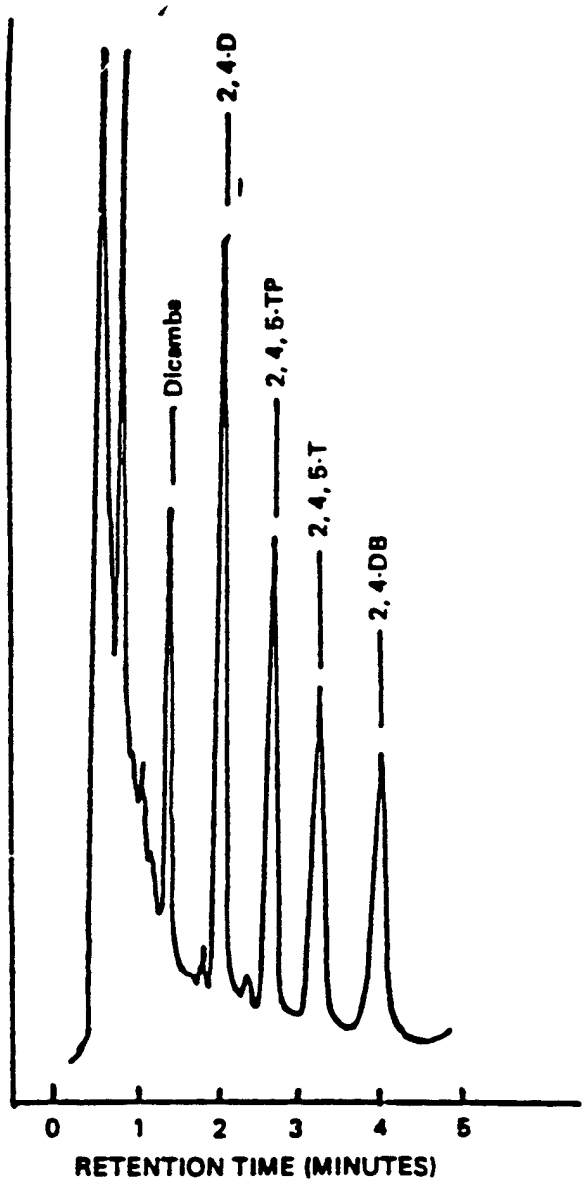


Figure 2. Gas chomatogram of chlorinated herbicides.

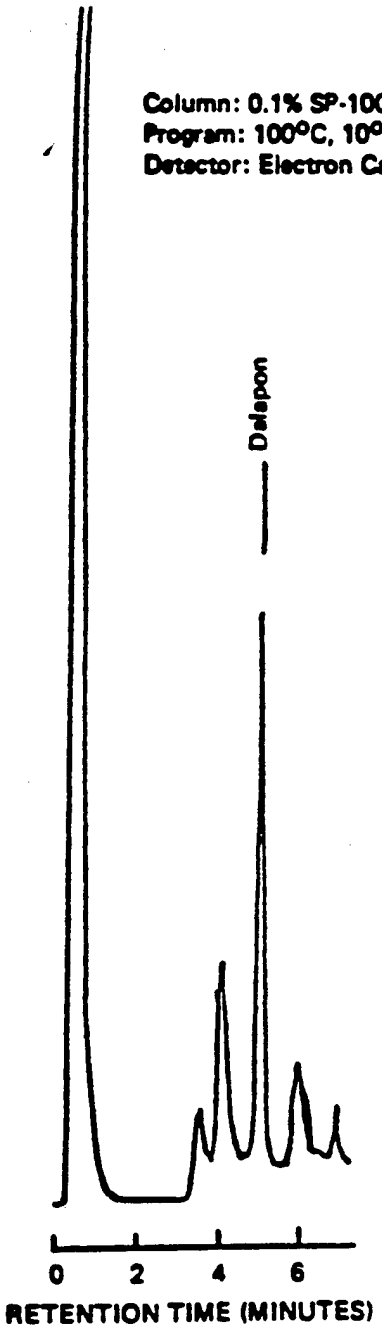


Figure 4. Gas chromatogram of dalapon, column 3.

9.0 METHOD PERFORMANCE

9.1 In a single laboratory, using reagent water and effluents from publicly owned treatment works (POTW), the average recoveries presented in Table 3 were obtained. The standard deviations of the percent recoveries of these measurements are also included in Table 3.

10.0 REFERENCES

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7. Eichelberger, J.W., L.E. Harris, and W.L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry," Analytical Chemistry, 47, 995, 1975.

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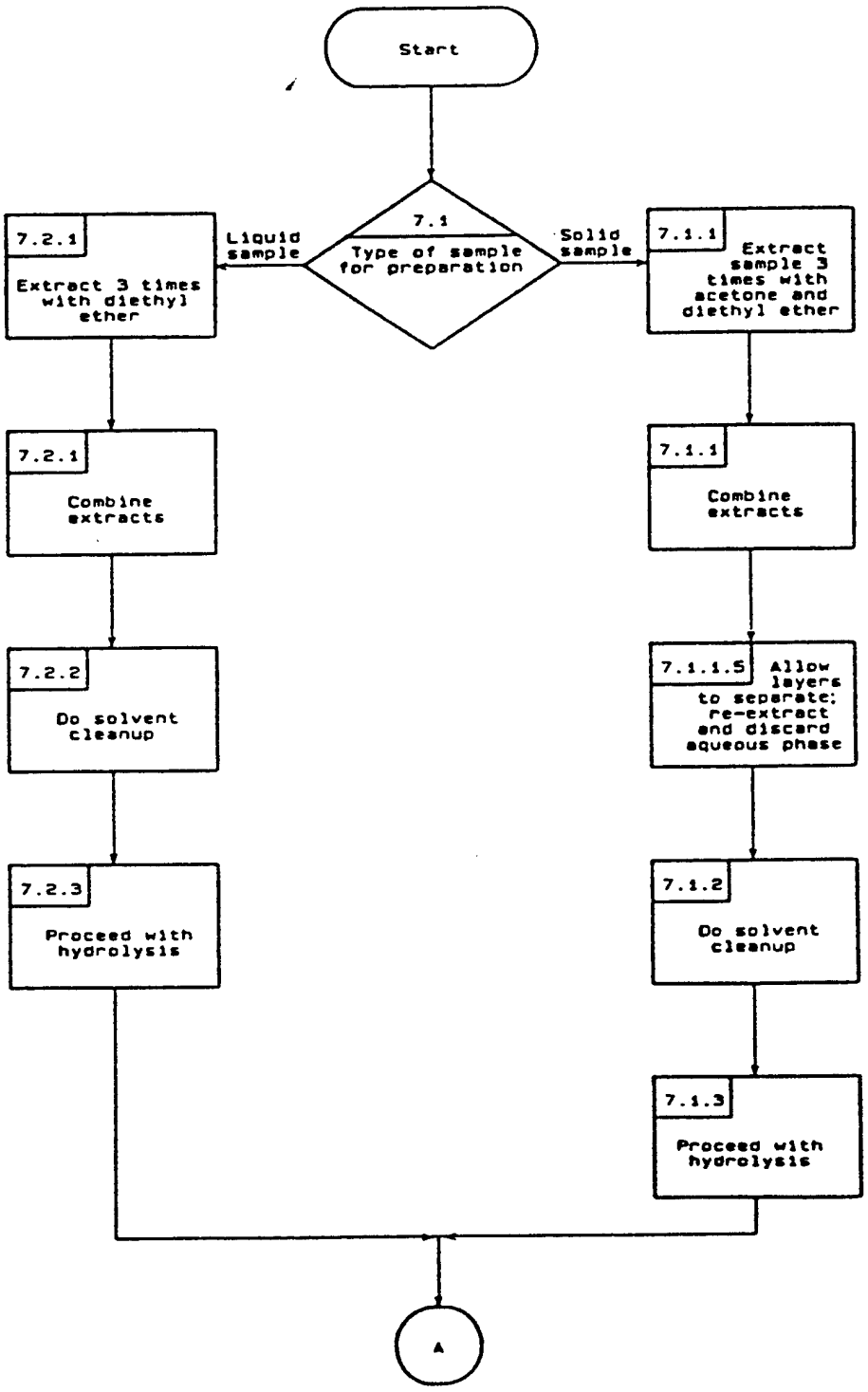
9. U.S. EPA, "Method 615. The Determination of Chlorinated Herbicides in Industrial and Municipal Wastewater," Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, 45268, June 1982.


Start
7.1
Type of sample for preparation
Liquid sample
Solid sample
7.2.1
Extract 3 times with diethyl ether
7.1.1
Extract sample 3 times with acetone and diethyl ether
7.2.1
Combine extracts
7.1.1
Combine extracts
7.2.2
Do solvent cleanup
7.1.1.5
Allow layers to separate; re-extract and discard aqueous phase
7.2.3
Proceed with hydrolysis
7.1.2
Do solvent cleanup
7.1.3
Proceed with hydrolysis
A

METHOD 3005

ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Method 3005 is an acid digestion procedure used to prepare surface water and ground water samples for analysis by flame atomic absorption spectroscopy (FAA) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by Method 3005 may be analyzed by AAS or ICP for the following metals:

Aluminum	Magnesium
Antimony	Manganese
Arsenic*	Molybdenum
Barium	Nickel
Beryllium	Potassium
Cadmium	Selenium*
Calcium	Silver
Chromium	Sodium
Cobalt	Thallium
Copper	Vanadium
Iron	Zinc
Lead	

*ICP only

1.2 For the analysis of total dissolved metals, the sample is filtered at the time of collection, prior to acidification with nitric acid.

2.0 SUMMARY OF METHOD

2.1 Total recoverable metals: The entire sample is acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is filtered and diluted to volume, and is then ready for analysis.

2.2 Dissolved metals: The sample is filtered through a 0.5 um filter at the time of collection and the liquid phase is then acidified at the time of collection with nitric acid. At the time of analysis the sample is heated with acid and substantially reduced in volume. The digestate is again filtered (if necessary) and diluted to volume and is then ready for analysis.

7.0 PROCEDURE

7.1 Transfer a 100-mL aliquot of well-mixed sample to a beaker.

7.2 For metals that are to be analyzed by FLAA or ICP, add 2 mL of concentrated HNO_3 and 5 mL of concentrated HCl. The sample is covered with a ribbed watch glass and heated on a steam bath or hot plate at 90 to 95°C until the volume has been reduced to 15-20 mL.

CAUTION: Do not boil. Antimony is easily lost by volatilization from hydrochloric acid media.

7.3 Remove the beaker and allow to cool. Wash down the beaker walls and watch glass with Type II water and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble material that could clog the nebulizer. Filtration should be done only if there is concern that insoluble materials may clog the nebulizer; this additional step is liable to cause sample contamination unless the filter and filtering apparatus are thoroughly cleaned and prerinsed with dilute HNO_3.

7.4 Adjust the final volume to 100 mL with Type II water.

8.0 QUALITY CONTROL

8.1 For each analytical batch of samples processed, blanks (Type II water and reagents) should be carried throughout the entire sample preparation and analytical process. These blanks will be useful in determining if samples are being contaminated.

8.2 Duplicate samples should be processed on a routine basis. A duplicate sample is a sample brought through the whole sample preparation and analytical process. Duplicate samples will be used to determine precision. The sample load will dictate the frequency, but 20% is recommended.

8.3 Spiked samples or standard reference materials should be employed to determine accuracy. A spiked sample should be included with each group of samples processed and whenever a new sample matrix is being analyzed.

9.0 METHOD PERFORMANCE

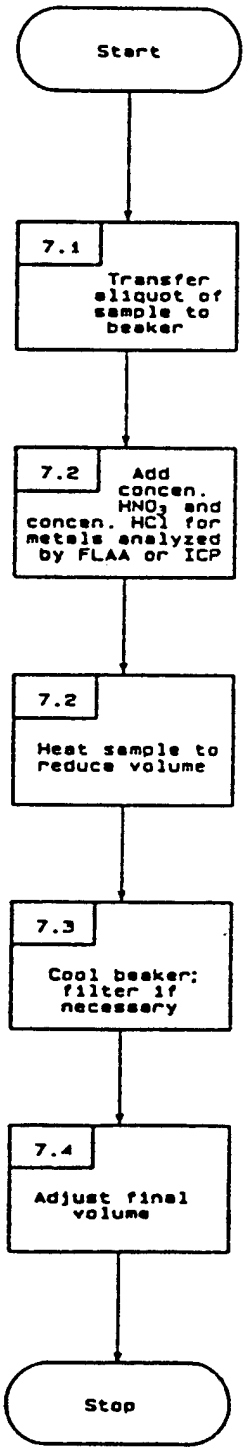
9.1 No data provided.

10.0 REFERENCES

10.1 None required.

METHOD 3005

ACID DIGESTION OF WATERS FOR TOTAL RECOVERABLE OR DISSOLVED METALS FOR ANALYSIS BY FLAA OR ICP SPECTROSCOPY



METHOD 3050

ACID DIGESTION OF SEDIMENTS, SLUDGES, AND SOILS

1.0 SCOPE AND APPLICATION

1.1 This method is an acid digestion procedure used to prepare sediments, sludges, and soil samples for analysis by flame or furnace atomic absorption spectroscopy (FLAA and GFAA, respectively) or by inductively coupled argon plasma spectroscopy (ICP). Samples prepared by this method may be analyzed by ICP for all the listed metals, or by FLAA or GFAA as indicated below (see also Paragraph 2.1):

FLAA		GFAA
Aluminum	Magnesium	Arsenic
Barium	Manganese	Beryllium
Beryllium	Molybdenum	Cadmium
Cadmium	Nickel	Chromium
Calcium	Potassium	Cobalt
Chromium	Sodium	Iron
Cobalt	Thallium	Molybdenum
Copper	Vanadium	Selenium
Iron	Zinc	Thallium
Lead		Vanadium

2.0 SUMMARY OF METHOD

2.1 A representative 1- to 2-g (wet weight) sample is digested in nitric acid and hydrogen peroxide. The digestate is then refluxed with either nitric acid or hydrochloric acid. Dilute hydrochloric acid is used as the final reflux acid for (1) the ICP analysis of As and Se, and (2) the flame AA or ICP analysis of Al, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Mo, Pb, Ni, K, Na, Tl, V, and Zn. Dilute nitric acid is employed as the final dilution acid for the furnace AA analysis of As, Be, Cd, Cr, Co, Pb, Mo, Se, Tl, and V. A separate sample shall be dried for a total solids determination.

3.0 INTERFERENCES

3.1 Sludge samples can contain diverse matrix types, each of which may present its own analytical challenge. Spiked samples and any relevant standard reference material should be processed to aid in determining whether Method 3050 is applicable to a given waste.

Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.

7.3 After Step 7.2 has been completed and the sample has cooled, add 2 mL of Type II water and 3 mL of 30% H_2O_2. Cover the beaker with a watch glass and return the covered beaker to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker.

7.4 Continue to add 30% H_2O_2 in 1-mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.
NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

7.5 If the sample is being prepared for (a) the ICP analysis of As and Se, or (b) the flame AA or ICP analysis of Al, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Mo, Ni, K, Na, Tl, V, and Zn, then add 5 mL of concentrated HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and reflux for an additional 15 min without boiling. After cooling, dilute to 100 mL with Type II water. Particulates in the digestate that may clog the nebulizer should be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.5.1 **Filtration:** Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.

7.5.2 **Centrifugation:** Centrifugation at 2,000-3,000 rpm for 10 min is usually sufficient to clear the supernatant.

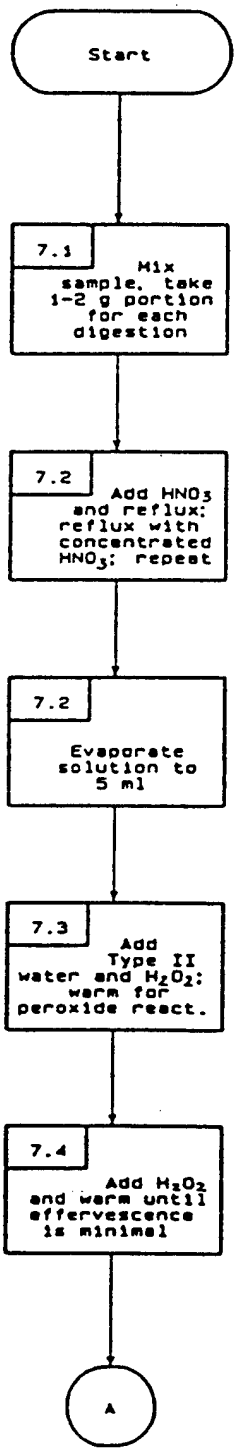
7.5.3 The diluted sample has an approximate acid concentration of 5.0% (v/v) HCl and 5.0% (v/v) HNO_3. The sample is now ready for analysis.

7.6 If the sample is being prepared for the furnace analysis of As, Be, Cd, Cr, Co, Pb, Mo, Se, Tl, and V, cover the sample with a ribbed watch glass and continue heating the acid-peroxide digestate until the volume has been reduced to approximately 5 mL. After cooling, dilute to 100 mL with Type II water. Particulates in the digestate should then be removed by filtration, by centrifugation, or by allowing the sample to settle.

7.6.1 **Filtration:** Filter through Whatman No. 41 filter paper (or equivalent) and dilute to 100 mL with Type II water.

7.6.2 **Centrifugation:** Centrifugation at 2,000-3,000 for 10 min is usually sufficient to clear the supernatant.

7.6.3 The diluted digestate solution contains approximately 5% (v/v) HNO_3. For analysis, withdraw aliquots of appropriate volume and add any required reagent or matrix modifier. The sample is now ready for analysis.


Start
7.1
Mix sample, take 1-2 g portion for each digestion
7.2
Add HNO_3 and reflux; reflux with concentrated HNO_3; repeat
7.2
Evaporate solution to 5 ml
7.3
Add Type II water and H_2O_2; warm for peroxide react.
7.4
Add H_2O_2 and warm until effervescence is minimal
A

3.3 METHODS FOR DETERMINATION OF METALS

This manual contains six analytical techniques for trace metal determinations: inductively coupled argon plasma emission spectrometry (ICP), direct-aspiration or flame atomic absorption spectrometry (FAA), graphite-furnace atomic absorption spectrometry (GFAA), hydride-generation atomic absorption spectrometry (HGAA), cold-vapor atomic absorption spectrometry (CVAA), and several procedures for hexavalent chromium analysis. Each of these is briefly discussed below in terms of advantages, disadvantages, and cautions for analysis of wastes.

ICP's primary advantage is that it allows simultaneous or rapid sequential determination of many elements in a short time. The primary disadvantage of ICP is background radiation from other elements and the plasma gases. Although all ICP instruments utilize high-resolution optics and background correction to minimize these interferences, analysis for traces of metals in the presence of a large excess of a single metal is difficult. Examples would be traces of metals in an alloy or traces of metals in a limed (high calcium) waste. ICP and Flame AA have comparable detection limits (within a factor of 4) except that ICP exhibits greater sensitivity for refractories (Al, Ba, etc.). Furnace AA, in general, will exhibit lower detection limits than either ICP or FLAA.

Flame AAS (FLAA) determinations, as opposed to ICP, are normally completed as single element analyses and are relatively free of interelement spectral interferences. Either a nitrous-oxide/acetylene or air/acetylene flame is used as an energy source for dissociating the aspirated sample into the free atomic state making analyte atoms available for absorption of light. In the analysis of some elements the temperature or type of flame used is critical. If the proper flame and analytical conditions are not used, chemical and ionization interferences can occur.

Graphite Furnace AAS (GFAA) replaces the flame with an electrically heated graphite furnace. The furnace allows for gradual heating of the sample aliquot in several stages. Thus, the processes of desolvation, drying, decomposition of organic and inorganic molecules and salts, and formation of atoms which must occur in a flame or ICP in a few milliseconds may be allowed to occur over a much longer time period and at controlled temperatures in the furnace. This allows an experienced analyst to remove unwanted matrix components by using temperature programming and/or matrix modifiers. The major advantage of this technique is that it affords extremely low detection limits. It is the easiest to perform on relatively clean samples. Because this technique is so sensitive, interferences can be a real problem; finding the optimum combination of digestion, heating times and temperatures, and matrix modifiers can be a challenge for complex matrices.

INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY

1.0 SCOPE AND APPLICATION

1.1 Inductively coupled plasma atomic emission spectroscopy (ICP) determines elements including metals in solution. The method is applicable to a large number of metals and wastes. All matrices, including ground water, aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes, require digestion prior to analysis.

1.2 Elements for which Method 6010 is applicable are listed in Table 1. Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of spectrometer. The data shown in Table 1 provide concentration ranges for clean aqueous samples. Use of this method is restricted to spectroscopists who are knowledgeable in the correction of spectral, chemical, and physical interferences.

1.3 The method of standard addition (MSA) (Paragraph 8.5.3) shall be used for the analysis of all EP extracts and sample digests unless either serial dilution or matrix spike addition demonstrates that it is not required.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, samples must be solubilized or digested using appropriate Sample Preparation Methods (e.g., Methods 3005-3050).

2.2 Method 6010 describes the simultaneous, or sequential, multielemental determination of elements by ICP. The method measures element-emitted light by optical spectrometry. Samples are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the lines are monitored by photomultiplier tubes. Background correction is required for trace element determination. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background-intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result. The possibility of additional interferences named in Section 3.0 should also be recognized and appropriate corrections made; tests for their presence are described in Section 8.5.

3.0 INTERFERENCES

3.1 Spectral interferences are caused by: (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomena; and (4) stray light from the line emission of high-concentration elements. Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multielement instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interferents can be assumed.

3.1.1 The interference is expressed as analyte concentration equivalents (i.e., false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined (at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The user is cautioned that other instruments may exhibit somewhat different levels of interference than those shown in Table 2. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, argon flow rate, etc.

3.1.2 The dashes in Table 2 indicate that no measurable interferences were observed even at higher interferent concentrations. Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

3.1.3 At present, information on the listed silver and potassium wavelengths is not available, but it has been reported that second-order energy from the magnesium 383.231-nm wavelength interferes with the listed potassium line at 766.491 nm.

3.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a

tip washer, or diluting the sample. Also, it has been reported that better control of the argon flow rate improves instrument performance; this is accomplished with the use of mass flow controllers.

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

4.0 APPARATUS AND MATERIALS

4.1 Inductively coupled argon plasma emission spectrometer:

4.1.1 Computer-controlled emission spectrometer with background correction.

4.1.2 Radio frequency generator.

4.1.3 Argon gas supply: Welding grade or better.

4.2 Operating conditions: The analyst should follow the instructions provided by the instrument's manufacturer. For operation with organic solvents, use of the auxiliary argon inlet is recommended, as are solvent-resistant tubing, increased plasma (coolant) argon flow, decreased nebulizer flow, and increased RF power to obtain stable operation and precise measurements. Sensitivity, instrumental detection limit, precision, linear dynamic range, and interference effects must be established for each individual analyte line on that particular instrument. All measurements must be within instrument linear range where coordination factors are valid. The analyst must (1) verify that the instrument configuration and operating conditions satisfy the analytical requirements and (2) maintain quality control data confirming instrument performance and analytical results.

5.0 REAGENTS

5.1 Acids used in the preparation of standards and for sample processing must be reagent grade or better. Redistilled acids may be used.

5.1.1 Concentrated hydrochloric acid (HCl).

5.1.2 Hydrochloric acid (1:1): Add 500 mL concentrated HCl to 400 mL Type II water and dilute to 1 liter.

5.1.3 Concentrated nitric acid (HNO_3).

5.1.4 Nitric acid (1:1): Add 500 mL concentrated HNO_3 to 400 mL Type II water and dilute to 1 liter.

5.3.6 **Boron solution**, stock 1 mL = 100 ug B: Do not dry. Dissolve 0.57 g anhydrous H_3BO_3 (mole fraction B = 0.1748), weighed accurately to at least four significant figures, in Type II water and dilute to 1,000 mL. Use a reagent meeting ACS specifications, keep the bottle tightly stoppered, and store in a desiccator to prevent the entrance of atmospheric moisture.

5.3.7 **Cadmium solution**, stock, 1 mL = 100 ug Cd: Dissolve 0.11 g CdO (mole fraction Cd = 0.8754), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.8 **Calcium solution**, stock, 1 mL = 100 ug Ca: Suspend 0.25 g $CaCO_3$ (mole Ca fraction = 0.4005), dried at 180°C for 1 hr before weighing, weighed accurately to at least four significant figures, in Type II water and dissolve cautiously with a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.9 **Chromium solution**, stock, 1 mL = 100 ug Cr: Dissolve 0.19 g CrO_3 (mole fraction Cr = 0.5200), weighed accurately to at least four significant figures, in Type II water. When solution is complete, acidify with 10 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.10 **Cobalt solution**, stock, 1 mL = 100 ug Co: Dissolve 0.1000 g of cobalt metal, weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) HCl and dilute to 1,000 mL with Type II water.

5.3.11 **Copper solution**, stock, 1 mL = 100 ug Cu: Dissolve 0.13 g CuO (mole fraction Cu = 0.7989), weighed accurately to at least four significant figures), in a minimum amount of (1:1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.12 **Iron solution**, stock, 1 mL = 100 ug Fe: Dissolve 0.14 g Fe_2O_3 (mole fraction Fe = 0.6994), weighed accurately to at least four significant figures, in a warm mixture of 20 mL (1:1) HCl and 2 mL of concentrated HNO_3. Cool, add an additional 5.0 mL of concentrated HNO_3, and dilute to 1,000 mL with Type II water.

5.3.13 **Lead solution**, stock, 1 mL = 100 ug Pb: Dissolve 0.16 g $Pb(NO_3)_2$ (mole fraction Pb = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10 mL (1:1) HNO_3 and dilute to 1,000 mL with Type II water.

5.3.14 **Magnesium solution**, stock, 1 mL = 100 ug Mg: Dissolve 0.17 g MgO (mole fraction Mg = 0.6030), weighed accurately to at least four significant figures, in a minimum amount of (1:1) HNO_3. Add 10.0 mL (1:1) concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.3.25 **Zinc solution**, stock, 1 mL = 100 ug Zn: Dissolve 0.12 g ZnO (mole fraction Zn = 0.8034), weighed accurately to at least four significant figures, in a minimum amount of dilute HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to 1,000 mL with Type II water.

5.4 Mixed calibration standard solutions: Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Table 3). Add 2 mL (1:1) HNO_3 and 10 mL of (1:1) HCl and dilute to 100 mL with Type II water (see NOTE, below). Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to FEP fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample (see Paragraph 5.8) and monitored weekly for stability. Some typical calibration standard combinations are listed in Table 3. All mixtures should then be scanned using a sequential spectrometer to verify the absence of interelement spectral interference in the recommended mixed standard solutions.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of Type II water and warm the flask until the solution clears. Cool and dilute to 100 mL with Type II water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional HCl.

TABLE 3. MIXED STANDARD SOLUTIONS

Solution	Elements
I	Be, Cd, Mn, Pb, Se and Zn
II	Ba, Co, Cu, Fe, and V
III	As, Mo, and Si
IV	Al, Ca, Cr, K, Na, and Ni
V	Ag (see Note to Paragraph 5.4), B, Mg, Sb, and Tl

7.2 Set up the instrument with proper operating parameters established in Paragraph 4.2. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 min of operation prior to calibration).

7.3 Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Paragraph 5.4. Flush the system with the calibration blank (5.5.1) between each standard (see NOTE, below). (Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error.)

NOTE: For boron concentrations greater than 500 ug/L, extended flush times of 1 or 2 min may be required.

7.4 Before beginning the sample run, reanalyze the highest mixed calibration standard as if it were a sample. Concentration values obtained should not deviate from the actual values by more than 5% (or the established control limits, whichever is lower). If they do, follow the recommendations of the instrument manufacturer to correct for this condition.

7.5 Flush the system with the calibration blank solution for at least 1 min (Paragraph 5.5.1) before the analysis of each sample (see Note to Paragraph 7.3). Analyze the instrument check standard (5.6) and the calibration blank (5.5.1) after each 10 samples.

7.6 Calculations: If dilutions were performed, the appropriate factors must be applied to sample values. All results should be reported in ug/L with up to three significant figures.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Dilute and reanalyze samples that are more concentrated than the linear calibration limit or use an alternate, less sensitive line for which quality control data is already established.

8.3 Employ a minimum of one laboratory blank per sample batch to determine if contamination or any memory effects are occurring.

8.4 Analyze one duplicate sample for every 20 samples. A duplicate sample is a sample brought through the whole sample preparation and analytical process.

8.5 It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests, as outlined in 8.5.1 through 8.5.3, will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values.

3. The interference effect must be constant over the working range of concern.

4. The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 1.

8.6 Check the instrument standardization by analyzing appropriate quality control check standards as follows.

8.6.1 Check instrument calibration using a calibration blank and two appropriate standards.

8.6.2 Verify calibration every 10 samples and at the end of the analytical run, using a calibration blank (5.5.1) and a single point check standard (5.6).

8.6.2.1 The results of the check standard are to agree within 10% of the expected value; if not, terminate the analysis, correct the problem, and recalibrate the instrument.

8.6.2.2 The results of the calibration blank are to agree within three standard deviations of the mean blank value. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem, recalibrate, and reanalyze the previous 10 samples.

8.6.3 Verify the interelement and background correction factors at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Do this by analyzing the interference check sample (Paragraph 5.7). Results should be within $\pm$20% of the true value obtained in 8.6.2.1.

8.6.4 Duplicate spiked samples are to be analyzed at a frequency of 20%.

8.6.4.1 The relative percent difference between duplicate determinations is to be calculated as follows:

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

where:

RPD = relative percent difference.
D_1 = first sample value.
D_2 = second sample value (duplicate).

(A control limit of ±20% for RPD shall be used for sample values greater than 10 times the instrument detection limit.)

8.6.4.2 The duplicate matrix spike sample recovery is to be within ±20% of the actual value.

8.6.5 The method of standard addition (Paragraph 8.5.3) shall be used for the analysis of all EP extracts.

9.0 METHOD PERFORMANCE

9.1 In an EPA round-robin Phase 1 study, seven laboratories applied the ICP technique to acid-distilled water matrices that had been spiked with various metal concentrates. Table 4 lists the true values, the mean reported values, and the mean percent relative standard deviations.

9.2 In a single laboratory evaluation, seven wastes were analyzed for 22 elements by this method. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was 9±2%. The mean percent recovery of spiked elements for all wastes was 93±6%. Spike levels ranged from 100 ug/L to 100 mg/L. The wastes included sludges and industrial wastewaters.

10.0 REFERENCES

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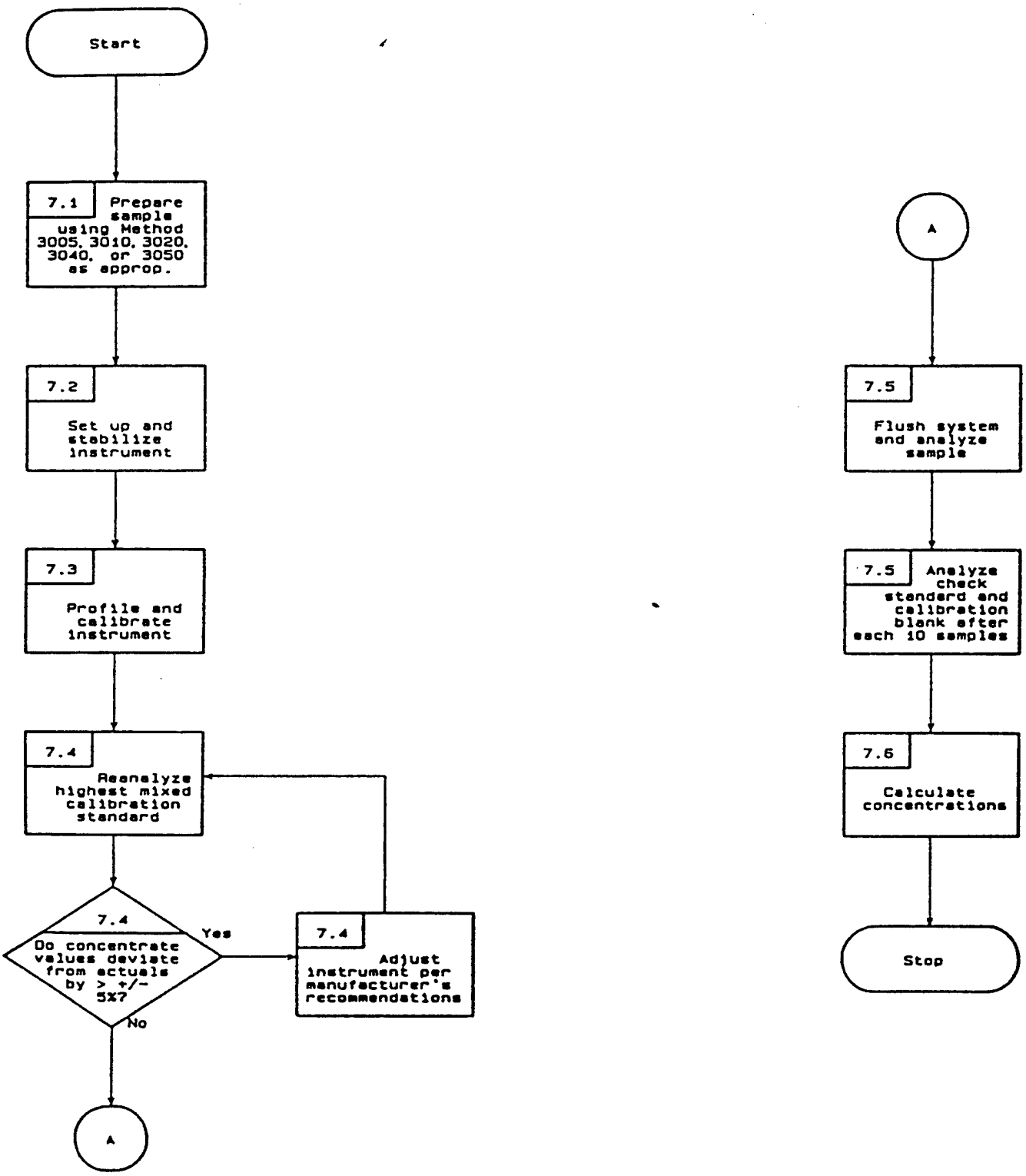
2. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-05, December 1982, Method 200.7.

3. Patel, B.K., Raab, G.A., et al., Report on a Single Laboratory Evaluation of Inductively Coupled Optical Emission Method 6010, EPA Contract No. 68-03-3050, December 1984.


Start
7.1 Prepare sample using Method 3005, 3010, 3020, 3040, or 3050 as approp.
7.2 Set up and stabilize instrument
7.3 Profile and calibrate instrument
7.4 Reanalyze highest mixed calibration standard
7.4 Do concentrate values deviate from actuals by > +/- 5%?
Yes
No
7.4 Adjust instrument per manufacturer's recommendations
A
A
7.5 Flush system and analyze sample
7.5 Analyze check standard and calibration blank after each 10 samples
7.6 Calculate concentrations
Stop

ATOMIC ABSORPTION METHODS

1.0 SCOPE AND APPLICATION

1.1 Metals in solution may be readily determined by atomic absorption spectroscopy. The method is simple, rapid, and applicable to a large number of metals in drinking, surface, and saline waters and domestic and industrial wastes. While drinking water free of particulate matter may be analyzed directly, ground water, other aqueous samples, EP extracts, industrial wastes, soils, sludges, sediments, and other solid wastes require digestion prior to analysis.

1.2 Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and models of atomic absorption spectrophotometers. The data shown in Table 1 provide some indication of the detection limits obtainable by direct aspiration and by furnace techniques. For clean aqueous samples, the detection limits shown in the table by direct aspiration may be extended downward with scale expansion and upward by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and/or through solvent extraction techniques. For certain samples, lower concentrations may also be determined using the furnace techniques. The detection limits given in Table 1 are somewhat dependent on equipment (such as the type of spectrophotometer and furnace accessory, the energy source, the degree of electrical expansion of the output signal), and are greatly dependent on sample matrix. When using furnace techniques, however, the analyst should be cautioned as to possible chemical reactions occurring at elevated temperatures which may result in either suppression or enhancement of the analysis element. To ensure valid data with furnace techniques, the analyst must examine each matrix for interference effects (see Paragraph 3.2.1) and, if detected, treat them accordingly, using either successive dilution, matrix modification, or method of standard additions (see Paragraph 8.7).

1.3 Where direct-aspiration atomic absorption techniques do not provide adequate sensitivity, reference is made to specialized procedures (in addition to the furnace procedure) such as the gaseous-hydride method for arsenic and selenium and the cold-vapor technique for mercury.

2.0 SUMMARY OF METHOD

2.1 Although methods have been reported for the analysis of solids by atomic absorption spectroscopy, the technique generally is limited to metals in solution or solubilized through some form of sample processing.

2.2 Preliminary treatment of waste water, ground water, EP extracts, and industrial waste is always necessary because of the complexity and

variability of sample matrix. Solids, slurries, and suspended material must be subjected to a solubilization process before analysis. This process may vary because of the metals to be determined and the nature of the sample being analyzed. Solubilization and digestion procedures are presented in Section 3.2 (Sample Preparation Methods).

2.3 In direct-aspiration atomic absorption spectroscopy, a sample is aspirated and atomized in a flame. A light beam from a hollow cathode lamp or an electrodeless discharge lamp is directed through the flame into a monochromator, and onto a detector that measures the amount of absorbed light. Absorption depends upon the presence of free unexcited ground-state atoms in the flame. Because the wavelength of the light beam is characteristic of only the metal being determined, the light energy absorbed by the flame is a measure of the concentration of that metal in the sample. This principle is the basis of atomic absorption spectroscopy.

2.4 When using the furnace technique in conjunction with an atomic absorption spectrophotometer, a representative aliquot of a sample is placed in the graphite tube in the furnace, evaporated to dryness, charred, and atomized. As a greater percentage of available analyte atoms is vaporized and dissociated for absorption in the tube rather than the flame, the use of smaller sample volumes or detection of lower concentrations of elements is possible. The principle is essentially the same as with direct aspiration atomic absorption, except that a furnace, rather than a flame, is used to atomize the sample. Radiation from a given excited element is passed through the vapor containing ground-state atoms of that element. The intensity of the transmitted radiation decreases in proportion to the amount of the ground-state element in the vapor. The metal atoms to be measured are placed in the beam of radiation by increasing the temperature of the furnace, thereby causing the injected specimen to be volatilized. A monochromator isolates the characteristic radiation from the hollow cathode lamp or electrodeless discharge lamp, and a photosensitive device measures the attenuated transmitted radiation.

3.0 INTERFERENCES

3.1 Direct aspiration:

3.1.1 The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule, as in the case of phosphate interference with magnesium, or when the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame. The addition of lanthanum will overcome phosphate interference in magnesium, calcium, and barium determinations. Similarly, silica interference in the determination of manganese can be eliminated by the addition of calcium.

1. Successively dilute and reanalyze the samples to eliminate interferences.

2. Modify the sample matrix either to remove interferences or to stabilize the analyte. Examples are the addition of ammonium nitrate to remove alkali chlorides and the addition of ammonium phosphate to retain cadmium. The mixing of hydrogen with the inert purge gas has also been used to suppress chemical interference. The hydrogen acts as a reducing agent and aids in molecular dissociation.

3. Analyze the sample by method of standard additions while noticing the precautions and limitations of its use (see Paragraph 8.7.2).

3.2.2 Gases generated in the furnace during atomization may have molecular absorption bands encompassing the analytical wavelength. When this occurs, use either background correction or choose an alternate wavelength. Background correction may also compensate for nonspecific broad-band absorption interference.

3.2.3 Continuum background correction cannot correct for all types of background interference. When the background interference cannot be compensated for, chemically remove the analyte or use an alternate form of background correction, e.g., Zeeman background correction.

3.2.4 Interference from a smoke-producing sample matrix can sometimes be reduced by extending the charring time at a higher temperature or utilizing an ashing cycle in the presence of air. Care must be taken, however, to prevent loss of the analyte.

3.2.5 Samples containing large amounts of organic materials should be oxidized by conventional acid digestion before being placed in the furnace. In this way, broad-band absorption will be minimized.

3.2.6 Anion interference studies in the graphite furnace indicate that, under conditions other than isothermal, the nitrate anion is preferred. Therefore, nitric acid is preferable for any digestion or solubilization step. If another acid in addition to HNO_3 is required, a minimum amount should be used. This applies particularly to hydrochloric and, to a lesser extent, to sulfuric and phosphoric acids.

3.2.7 Carbide formation resulting from the chemical environment of the furnace has been observed. Molybdenum may be cited as an example. When carbides form, the metal is released very slowly from the resulting metal carbide as atomization continues. Molybdenum may require 30 sec or more atomization time before the signal returns to baseline levels. Carbide formation is greatly reduced and the sensitivity increased with the use of pyrolytically coated graphite. Elements that readily form carbides are noted with the symbol (p) in Table 1.

water, and Type II water. (Chromic acid should not be used as a cleaning agent for glassware if chromium is to be included in the analytical scheme.) If it can be documented through an active analytical quality control program using spiked samples and reagent blanks that certain steps in the cleaning procedure are not required for routine samples, those steps may be eliminated from the procedure.

5.0 REAGENTS

5.1 Type II water (ASTM D1193): Use Type II water for the preparation of all reagents and calibration standards and as dilution water.

5.2 Concentrated nitric acid (HNO_3): Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with Type II water by adding the concentrated acid to an equal volume of water.

5.3 Hydrochloric acid (HCl, 1:1): Use a spectrograde acid certified for AA use. Prepare a 1:1 dilution with Type II water by adding the concentrated acid to an equal volume of water.

5.4 Fuel and oxidant: Commercial grade acetylene is generally acceptable. Air may be supplied from a compressed air line, a laboratory compressor, or a cylinder of compressed air. Reagent grade nitrous oxide is also required for certain determinations. Standard, commercially available argon and nitrogen are required for furnace work.

5.5 Stock standard metal solutions: Stock standard solutions are prepared from high purity metals, oxides, or nonhygroscopic reagent-grade salts using Type II water and redistilled nitric or hydrochloric acids. (See individual methods for specific instructions.) Sulfuric or phosphoric acids should be avoided as they produce an adverse effect on many elements. The stock solutions are prepared at concentrations of 1,000 mg of the metal per liter. Commercially available standard solutions may also be used. Where the sample viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition (MSA) may be used (see Paragraph 8.7).

5.6 Calibration standards: For those instruments which do not read out directly in concentration, a calibration curve is prepared to cover the appropriate concentration range. Usually, this means the preparation of standards which produce an absorbance of 0.0 to 0.7. Calibration standards are prepared by diluting the stock metal solutions at the time of analysis. For best results, calibration standards should be prepared fresh each time a batch of samples is analyzed. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range of the linear part of the curve. The calibration standards should be prepared using the same type of acid or combination of acids and at the same concentration as will result in the samples following processing. Beginning with the blank and working

7.3.2 Background correction is important when using flameless atomization, especially below 350 nm. Certain samples, when atomized, may absorb or scatter light from the lamp. This can be caused by the presence of gaseous molecular species, salt particles, or smoke in the sample beam. If no correction is made, sample absorbance will be greater than it should be, and the analytical result will be erroneously high. Zeeman background correction is effective in overcoming composition or structured background interferences. It is particularly useful when analyzing for As in the presence of Al and when analyzing for Se in the presence of Fe.

7.3.3 Memory effects occur when the analyte is not totally volatilized during atomization. This condition depends on several factors: volatility of the element and its chemical form, whether pyrolytic graphite is used, the rate of atomization, and furnace design. This situation is detected through blank burns. The tube should be cleaned by operating the furnace at full power for the required time period, as needed, at regular intervals during the series of determinations.

7.3.4 Inject a measured microliter aliquot of sample into the furnace and atomize. If the concentration found is greater than the highest standard, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

7.3.5 To verify the absence of interference, follow the serial dilution procedure given in Paragraph 8.6.

7.3.6 A check standard should be run after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or significant change in the signal for the standard indicates that the tube should be replaced. Tube life depends on sample matrix and atomization temperature. A conservative estimate would be that a tube will last at least 50 firings. A pyrolytic coating will extend that estimated life by a factor of three.

7.4 Calculation:

7.4.1 For determination of metal concentration by direct aspiration and furnace: Read the metal value in ug/L from the calibration curve or directly from the read-out system of the instrument.

7.4.2 If dilution of sample was required:

$$\text{ug/L metal in sample} = A \left(\frac{C + B}{C}\right)$$

8.5 Where the sample matrix is so complex that viscosity, surface tension, and components cannot be accurately matched with standards, the method of standard addition may be used (see Section 8.7 below).

8.6 Serial dilution: Withdraw from the sample two equal aliquots. To one of the aliquots add a known amount of analyte and dilute both aliquots to the same predetermined volume. (The dilution volume should be based on the analysis of the undiluted sample. Preferably, the dilution should be 1:4, while keeping in mind that the diluted value should be at least 5 times the instrument detection limit. Under no circumstances should the dilution be less than 1:1.) The diluted aliquots should then be analyzed, and the unspiked results, multiplied by the dilution factor, should be compared to the original determination. Agreement of the results (within 10%) indicates the absence of interference. Comparison of the actual signal from the spike with the expected response from the analyte in an aqueous standard should help confirm the finding from the dilution analysis.

8.7 Method of standard additions:

8.7.1 In the simplest version of this method, equal volumes of sample are added to a deionized distilled (Type II) water blank and to a standard (refer to Paragraph 8.7.3). If a higher degree of accuracy is required, more than one addition should be made. The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown in Figure 1.

8.7.2 The method of standard additions can be very useful; however, for the results to be valid the following limitations must be taken into consideration:

a. The absorbance plot of sample and standards must be linear over the concentration range of concern. For best results, the slope of the plot should be nearly the same as the slope of the aqueous standard curve. If the slope is significantly different (more than 20%), caution should be exercised.

b. The effect of the interference should not vary as the ratio of analyte concentration to sample matrix changes, and the standard addition should respond in a similar manner as the analyte.

c. The determination must be free of spectral interference and corrected for nonspecific background interference.

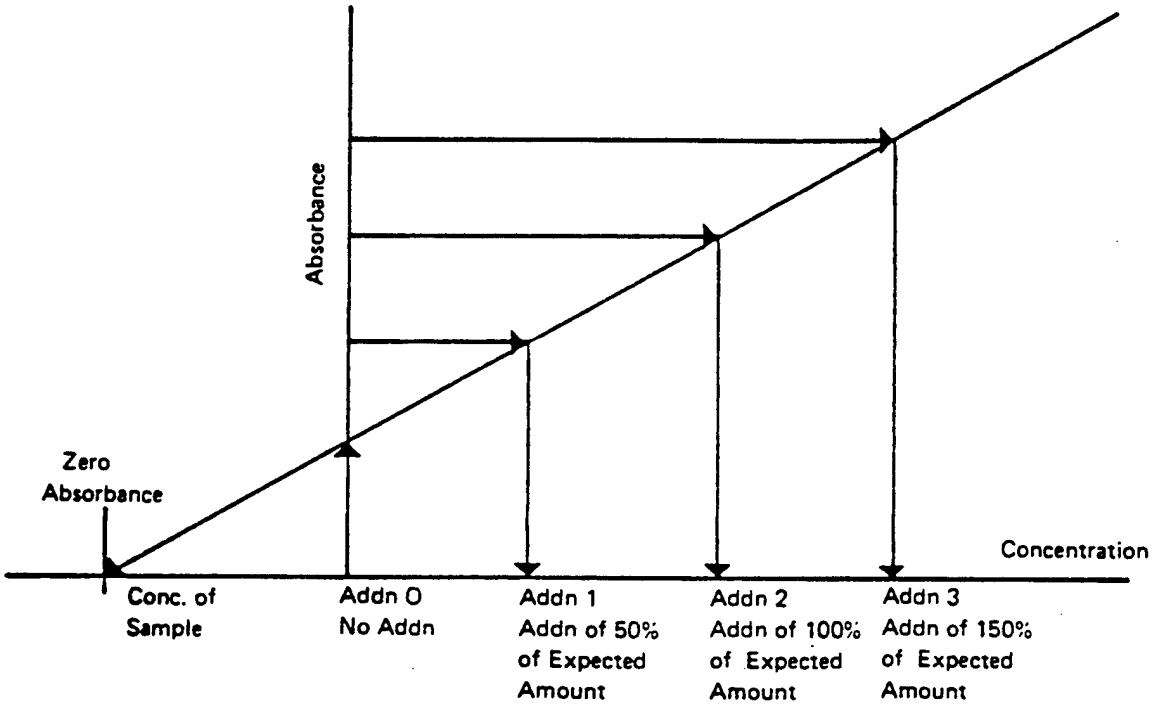
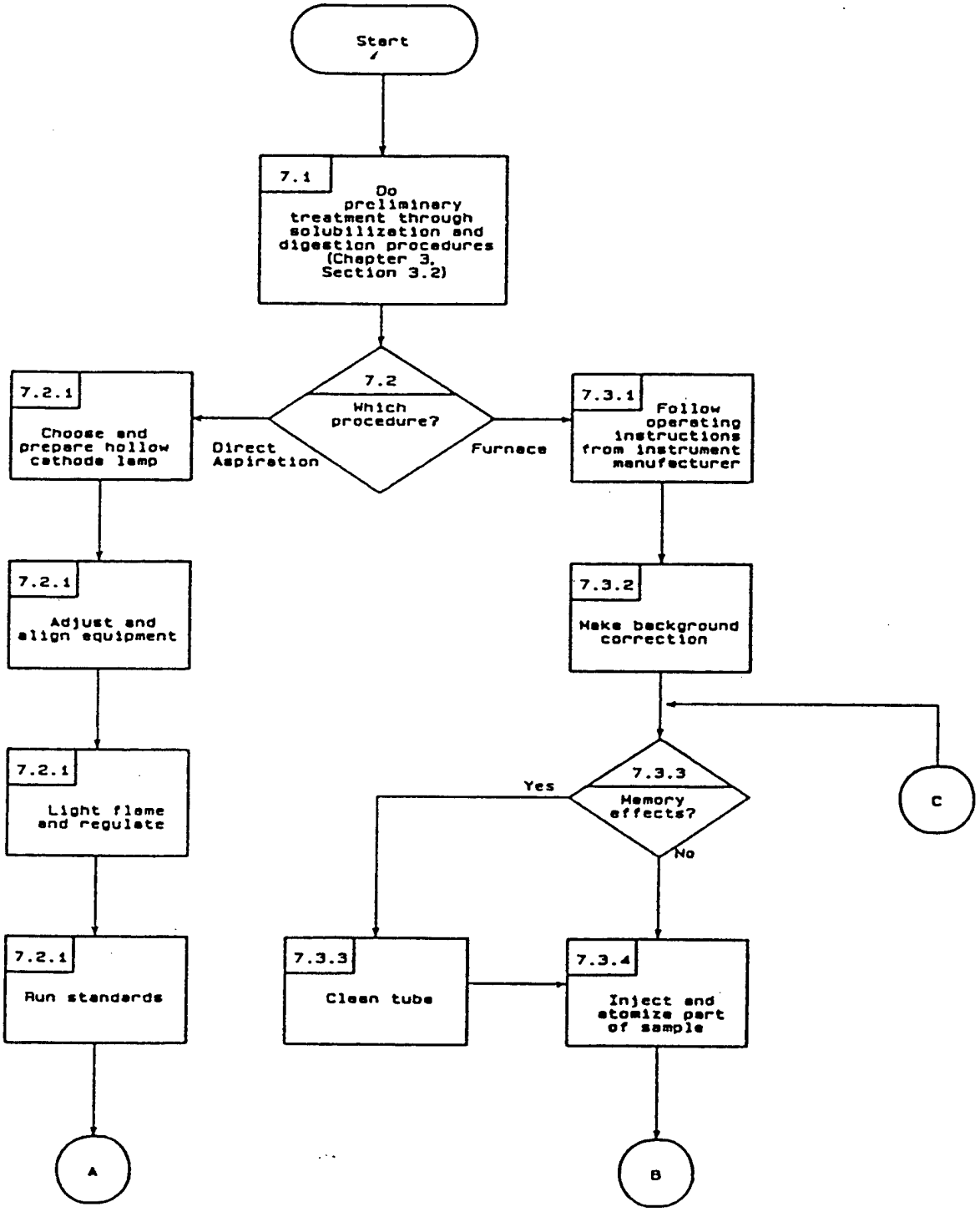


Figure 1. Standard Addition Plot.


Start
7.1
Do preliminary treatment through solubilization and digestion procedures (Chapter 3, Section 3.2)
7.2
Which procedure?
Direct Aspiration
Furnace
7.2.1
Choose and prepare hollow cathode lamp
7.2.1
Adjust and align equipment
7.2.1
Light flame and regulate
7.2.1
Run standards
A
7.3.1
Follow operating instructions from instrument manufacturer
7.3.2
Make background correction
7.3.3
Memory effects?
Yes
No
C
7.3.3
Clean tube
7.3.4
Inject and atomize part of sample
B

MERCURY IN LIQUID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7470 is a cold-vapor atomic absorption procedure approved for determining the concentration of mercury in mobility-procedure extracts, aqueous wastes, and ground waters. (Method 7470 can also be used for analyzing certain solid and sludge-type wastes; however, Method 7471 is usually the method of choice for these waste types.) All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the liquid samples must be prepared according to the procedure discussed in this method.

2.2 Method 7470, a cold-vapor atomic absorption technique, is based on the absorption of radiation at 253.7-nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

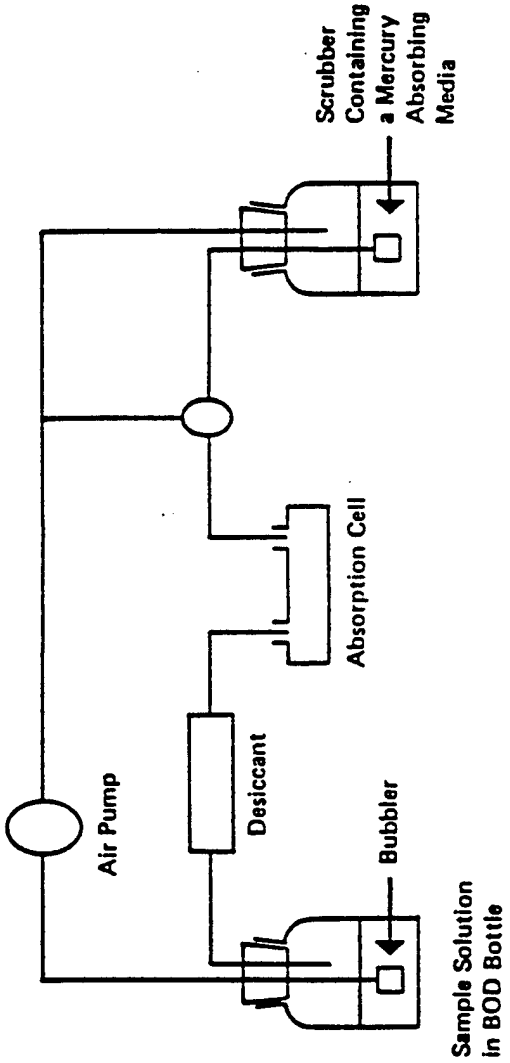


Figure 1. Apparatus for flameless mercury determination.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with HNO_3. The suggested maximum holding times for these samples are 38 days in glass containers and 13 days in plastic containers.

6.4 Nonaqueous samples shall be refrigerated, when possible, and analyzed as soon as possible.

7.0 PROCEDURE

7.1 Sample preparation: Transfer 100 mL, or an aliquot diluted to 100 mL, containing <1.0 g of mercury, to a 300-mL BOD bottle. Add 5 mL of H_2SO_4 and 2.5 mL of concentrated HNO_3, mixing after each addition. Add 15 mL of potassium permanganate solution to each sample bottle. Sewage samples may require additional permanganate. Ensure that equal amounts of permanganate are added to standards and blanks. Shake and add additional portions of potassium permanganate solution, if necessary, until the purple color persists for at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After a delay of at least 30 sec, add 5 mL of stannous sulfate, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

7.2 Standard preparation: Transfer 0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10.0-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles. Add enough Type II water to each bottle to make a total volume of 100 mL. Mix thoroughly and add 5 mL of concentrated H_2SO_4 and 2.5 mL of concentrated HNO_3 to each bottle. Add 15 mL of $KMnO_4$ solution to each bottle and allow to stand at least 15 min. Add 8 mL of potassium persulfate to each bottle and heat for 2 hr in a water bath maintained at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. When the solution has been decolorized, wait 30 sec, add 5 mL of the stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Paragraph 7.3.

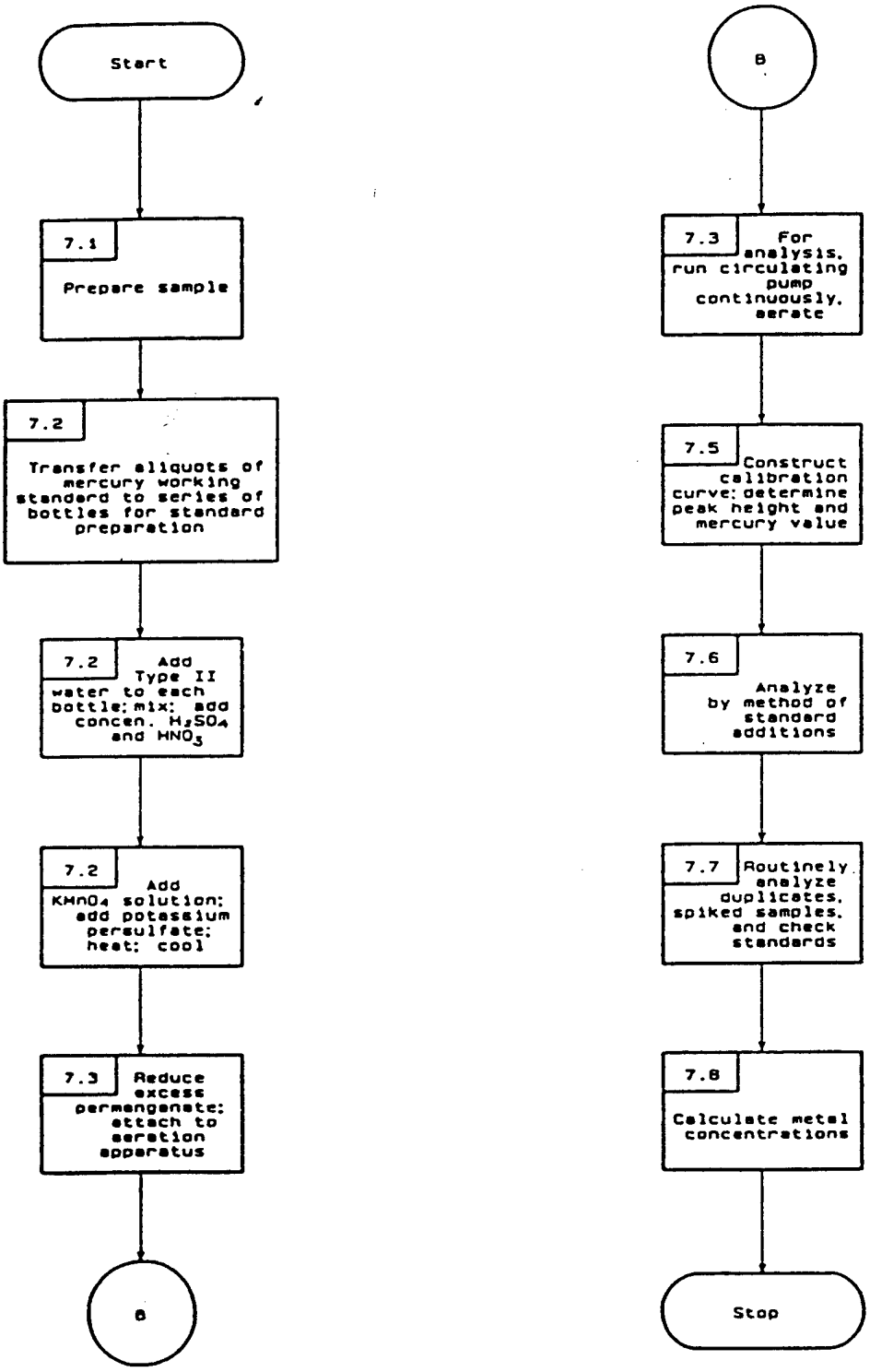
7.3 Analysis: At this point the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 liter/min, is allowed to run continuously. The absorbance will increase and reach a maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and

9.0 METHOD PERFORMANCE

9.1 Precision and accuracy data are available in Method 245.1 of Methods for Chemical Analysis of Water and Wastes.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.1.


Start
7.1 Prepare sample
7.2 Transfer aliquots of mercury working standard to series of bottles for standard preparation
7.2 Add Type II water to each bottle; mix; add concen. H_2SO_4 and HNO_3
7.2 Add $KMnO_4$ solution; add potassium persulfate; heat; cool
7.3 Reduce excess permanganate; attach to aeration apparatus
B
B
7.3 For analysis, run circulating pump continuously, aerate
7.5 Construct calibration curve; determine peak height and mercury value
7.6 Analyze by method of standard additions
7.7 Routinely analyze duplicates, spiked samples, and check standards
7.8 Calculate metal concentrations
Stop

MERCURY IN SOLID OR SEMISOLID WASTE (MANUAL COLD-VAPOR TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis.

2.0 SUMMARY OF METHOD

2.1 Prior to analysis, the solid or semi-solid samples must be prepared according to the procedures discussed in this method.

2.2 Method 7471, a cold-vapor atomic absorption method, is based on the absorption of radiation at the 253.7-nm wavelength by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) is measured as a function of mercury concentration.

2.3 The typical detection limit for this method is 0.0002 mg/L.

3.0 INTERFERENCES

3.1 Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/L of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from Type II water.

3.2 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L had no effect on recovery of mercury from spiked samples.

3.3 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 mL) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253 nm. Care must therefore be taken to ensure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). In addition, the dead air space in the BOD bottle must be purged before adding stannous sulfate. Both inorganic and organic mercury spikes have been quantitatively recovered from seawater by using this technique.

3.4 Certain volatile organic materials that absorb at this wavelength may also cause interference. A preliminary run without reagents should determine if this type of interference is present.

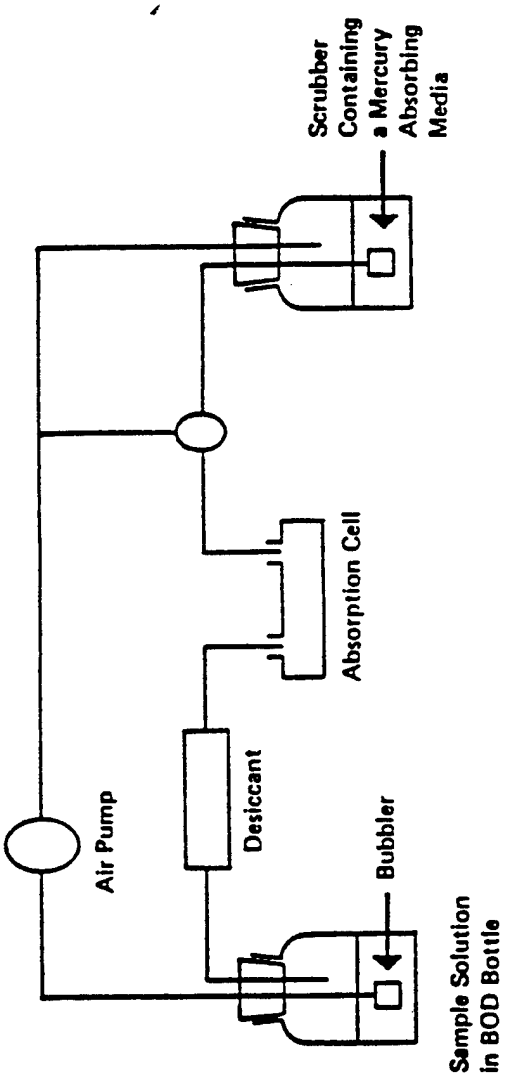


Figure 1. Apparatus for flameless mercury determination.

6.2 All sample containers must be prewashed with detergents, acids, and Type II water. Plastic and glass containers are both suitable.

6.3 Aqueous samples must be acidified to a pH <2 with nitric acid.

6.4 For solids or semisolids, moisture may be driven off in a drying oven at a temperature of 60°C.

7.0 PROCEDURE

7.1 Sample preparation: Weigh triplicate 0.2-g portions of untreated sample and place in the bottom of a BOD bottle. Add 5 mL of Type II water and 5 mL of aqua regia. Heat 2 min in a water bath at 95°C. Cool; then add 50 mL Type II water and 15 mL potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 min at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate.

CAUTION: Do this addition under a hood, as Cl_2 could be evolved. Add 55 mL of Type II water. Treating each bottle individually, add 5 mL of stannous sulfate and immediately attach the bottle to the aeration apparatus. Continue as described under step 7.4.

7.2 An alternate digestion procedure employing an autoclave may also be used. In this method, 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 are added to the 0.2 g of sample. Add 5 mL of saturated $KMnO_4$ solution and cover the bottle with a piece of aluminum foil. The samples are autoclaved at 121°C and 15 lb for 15 min. Cool, dilute to a volume of 100 mL with Type II water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Purge the dead air space and continue as described under step 7.4.

7.3 Standard preparation: Transfer 0.0-, 0.5-, 1.0-, 2.0-, 5.0-, and 10-mL aliquots of the mercury working standard, containing 0-1.0 ug of mercury, to a series of 300-mL BOD bottles. Add enough Type II water to each bottle to make a total volume of 10 mL. Add 5 mL of aqua regia and heat 2 min in a water bath at 95°C. Allow the sample to cool; add 50 mL Type II water and 15 mL of $KMnO_4$ solution to each bottle and return to the water bath for 30 min. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. Add 50 mL of Type II water. Treating each bottle individually, add 5 mL of stannous sulfate solution, immediately attach the bottle to the aeration apparatus, and continue as described in Step 7.4.

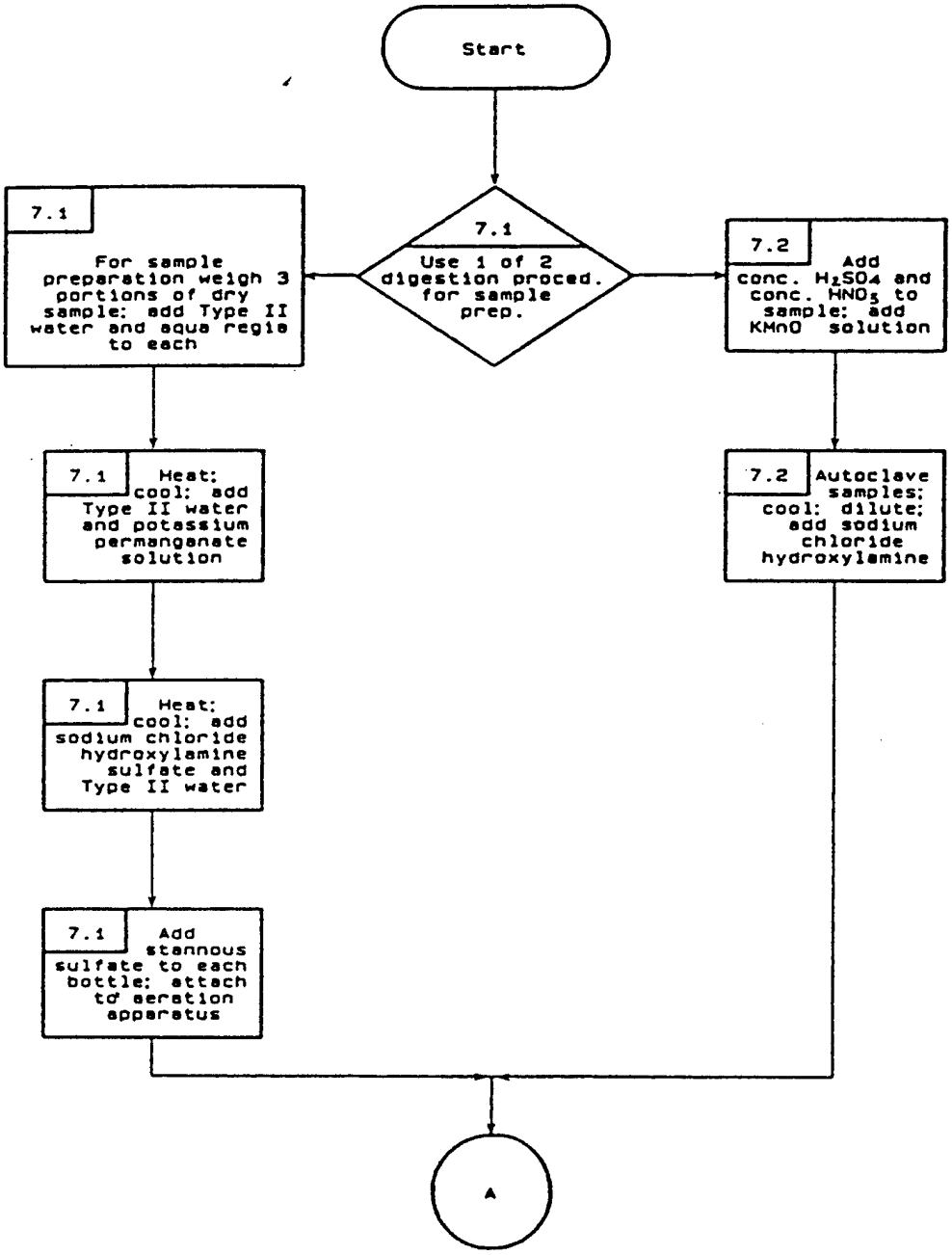
7.4 Analysis: At this point, the sample is allowed to stand quietly without manual agitation. The circulating pump, which has previously been adjusted to a rate of 1 L/min, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 sec. As soon as the recorder pen levels off (approximately 1 min), open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle, and continue the aeration.

9.2 The data shown in Table 1 were obtained from records of state and contractor laboratories. The data are intended to show the precision of the combined sample preparation and analysis method.

10.0 REFERENCES

1. Methods for Chemical Analysis of Water and Wastes, EPA-600/4-82-055, December 1982, Method 245.5.

2. Gaskill, A., Compilation and Evaluation of RCRA Method Performance Data, Work Assignment No. 2, EPA Contract No. 68-01-7075, September 1986.


Start
7.1
Use 1 of 2 digestion proced. for sample prep.
7.1
For sample preparation weigh 3 portions of dry sample; add Type II water and aqua regia to each
7.2
Add conc. H_2SO_4 and conc. HNO_3 to sample; add KMnO solution
7.1
Heat; cool; add Type II water and potassium permanganate solution
7.2
Autoclave samples; cool; dilute; add sodium chloride hydroxylamine
7.1
Heat; cool; add sodium chloride hydroxylamine sulfate and Type II water
7.1
Add stannous sulfate to each bottle; attach to aeration apparatus
A

METHOD 7841

THALLIUM (ATOMIC ABSORPTION, FURNACE TECHNIQUE)

1.0 SCOPE AND APPLICATION

1.1 See Section 1.0 of Method 7000.

2.0 SUMMARY OF METHOD

2.1 See Section 2.0 of Method 7000.

3.0 INTERFERENCES

3.1 See Section 3.0 of Method 7000 if interferences are suspected.

3.2 Background correction is required.

3.3 Hydrochloric acid or excessive chloride will cause volatilization of thallium at low temperatures. Verification that losses are not occurring, by spiked samples or standard additions, must be made for each sample matrix.

3.4 Palladium is a suitable matrix modifier for thallium analysis.

4.0 APPARATUS AND MATERIALS

4.1 For basic apparatus, see Section 4.0 of Method 7000.

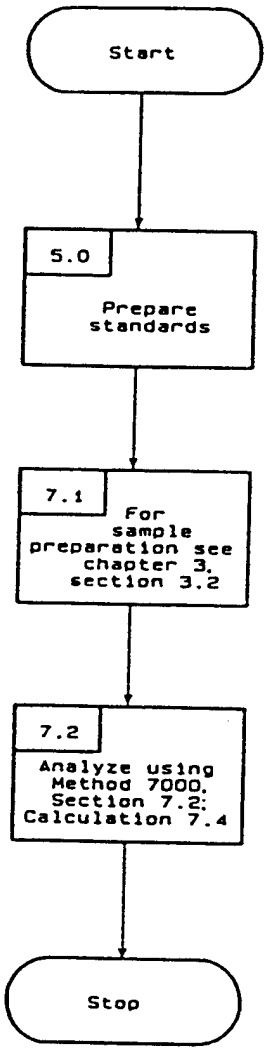
4.2 Instrument parameters (general):

4.2.1 **Drying time and temp:** 30 sec at 125°C.
4.2.2 **Ashing time and temp:** 30 sec at 400°C.
4.2.3 **Atomizing time and temp:** 10 sec at 2400°C.
4.2.4 **Purge gas:** Argon or nitrogen.
4.2.5 **Wavelength:** 276.8 nm.
4.2.6 **Background correction:** Required.
4.2.7 Other operating parameters should be set as specified by the particular instrument manufacturer.

NOTE: The above concentration values and instrument conditions are for a Perkin-Elmer HGA-2100, based on the use of a 20-uL injection, continuous-flow purge gas, and nonpyrolytic graphite. Smaller sizes of furnace devices or those employing faster rates of atomization can be operated using lower atomization temperatures for shorter time periods than the above-recommended settings.

10.0 REFERENCES

1. Application of Matrix-Modification in Determination of Thallium in Wastewater by Graphite-Furnace Atomic-Absorption Spectrometry, Talanta, 31(2) (1984), pp. 150-152.


Start
5.0
Prepare standards
7.1
For sample preparation see chapter 3, section 3.2
7.2
Analyze using Method 7000, Section 7.2; Calculation 7.4
Stop

RESIDUE, NON-FILTERABLE

Method 160.2 (Gravimetric, Dried at 103–105°C)

STORET NO. 00530

1. Scope and Application
   1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.
   1.2 The practical range of the determination is 4 mg/1 to 20,000 mg/1.
2. Summary of Method
   2.1 A well-mixed sample is filtered through a glass fiber filter, and the residue retained on the filter is dried to constant weight at 103–105°C.
   2.2 The filtrate from this method may be used for Residue, Filterable.
3. Definitions
   3.1 Residue, non-filterable, is defined as those solids which are retained by a glass fiber filter and dried to constant weight at 103–105°C.
4. Sample Handling and Preservation
   4.1 Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.
   4.2 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration or icing to 4°C, to minimize microbiological decomposition of solids, is recommended.
5. Interferences
   5.1 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because these variables have been shown to affect the results.
   5.2 Samples high in Filterable Residue (dissolved solids), such as saline waters, brines and some wastes, may be subject to a positive interference. Care must be taken in selecting the filtering apparatus so that washing of the filter and any dissolved solids in the filter (7.5) minimizes this potential interference.
6. Apparatus
   6.1 Glass fiber filter discs, without organic binder, such as Millipore AP-40, Reeves Angel 934-AH, Gelman type A/E, or equivalent.
   NOTE: Because of the physical nature of glass fiber filters, the absolute pore size cannot be controlled or measured. Terms such as "pore size", collection efficiencies and effective retention are used to define this property in glass fiber filters. Values for these parameters vary for the filters listed above.
   6.2 Filter support: filtering apparatus with reservoir and a coarse (40–60 microns) fritted disc as a filter support.

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Issued 1971

7.6 Carefully remove the filter from the filter support. Alternatively, remove crucible and filter from crucible adapter. Dry at least one hour at 103–105°C. Cool in a desiccator and weigh. Repeat the drying cycle until a constant weight is obtained (weight loss is less than 0.5 mg).

8. Calculations

8.1 Calculate non-filterable residue as follows:

$$\text{Non-filterable residue, mg/l} = \frac{(A - B)\times 1{,}000}{C}$$

where:

A = weight of filter (or filter and crucible) + residue in mg
B = weight of filter (or filter and crucible) in mg
C = ml of sample filtered

9. Precision and Accuracy

9.1 Precision data are not available at this time.

9.2 Accuracy data on actual samples cannot be obtained.

Bibliography

1. NCASI Technical Bulletin No. 291, March 1977. National Council of the Paper Industry for Air and Stream Improvement, Inc., 260 Madison Ave., NY.

HARDNESS, Total (mg/1 as $CaCO_3$)

Method 130.1 (Colorimetric, Automated EDTA)

STORET NO. 00900

1. Scope and Application
   1.1 This automated method is applicable to drinking, surface, and saline waters. The applicable range is 10 to 400 mg/1 as $CaCO_3$. Approximately 12 samples per hour can be analyzed.
2. Summary of Method
   2.1 The magnesium EDTA exchanges magnesium on an equivalent basis for any calcium and/or other cations to form a more stable EDTA chelate than magnesium. The free magnesium reacts with calmagite at a pH of 10 to give a red-violet complex. Thus, by measuring only magnesium concentration in the final reaction stream, an accurate measurement of total hardness is possible.
3. Sample Handling and Preservation
   3.1 Cool to 4°C, HNO_3 to pH < 2.
4. Interferences
   4.1 No significant interferences.
5. Apparatus
   5.1 Technicon AutoAnalyzer consisting of:
      5.1.1 Sampler I.
      5.1.2 Continuous Filter.
      5.1.3 Manifold.
      5.1.4 Proportioning Pump.
      5.1.5 Colorimeter equipped with 15 mm tubular flow cell and 520 nm filters.
      5.1.6 Recorder equipped with range expander.
6. Reagents
   6.1 Buffer: Dissolve 67.6 g NH_4Cl in 572 ml of NH_4OH and dilute to 1 liter with distilled water.
   6.2 Calmagite Indicator: Dissolve 0.25 g in 500 ml of distilled water by stirring approximately 30 minutes on a magnetic stirrer. Filter.
   6.3 Monomagnesium ethylenediamine-tetraacetate (MgEDTA): Dissolve 0.2 g of MgEDTA in 1 liter of distilled water.
   6.4 Stock Solution: Weigh 1.000 g of calcium carbonate (pre-dried at 105°C) into 500 ml Erlenmeyer flask; add 1:1 HCl until all $CaCO_3$ has dissolved. Add 200 ml of distilled water and boil for a few minutes. Cool, add a few drops of methyl red indicator, and adjust to the orange color with 3N NH_4OH and dilute to 1000 ml with distilled water. 1.0 ml = 1.0 mg $CaCO_3$.

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Issued 1971

9. Precision and Accuracy

9.1 In a single laboratory (EMSL), using surface water samples at concentrations of 19, 120, 385, and 366 mg/1 as $CaCO_3$, the standard deviations were ±1.5, ±1.5, ±4.5, and ±5.0, respectively.

9.2 In a single laboratory (EMSL), using surface water samples at concentrations of 39 and 296 mg/1 as $CaCO_3$, recoveries were 89% and 93%, respectively.

Bibliography

1. Technicon AutoAnalyzer Methodology, Bulletin No. 2, Technicon Controls, Inc., Chauncey, New York (July 1960).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 202, Method 309B (1975).

PETROLEUM HYDROCARBONS, TOTAL RECOVERABLE

Method 418.1 (Spectrophotometric, Infrared)

STORET NO. 45501

1. Scope and Application
   - 1.1 This method is for the measurement of fluorocarbon-113 extractable petroleum hydrocarbons from surface and saline waters, industrial and domestic wastes.
   - 1.2 The method is applicable to measurement of light fuels, although loss of about half of any gasoline present during the extraction manipulations can be expected.
   - 1.3 The method is sensitive to levels of 1 mg/1 and less, and may be extended to ambient monitoring.
2. Summary of Method
   - 2.1 The sample is acidified to a low pH (< 2) and serially extracted with fluorocarbon-113 in a separatory funnel. Interferences are removed with silica gel adsorbant. Infrared analysis of the extract is performed by direct comparison with standards.
3. Definitions
   - 3.1 As in the case of Oil and Grease, the parameter of Petroleum Hydrocarbons is defined by the method. The measurement may be subject to interferences and the results should be evaluated accordingly.
   - 3.2 Oil and Grease is a measure of biodegradable animal greases and vegetable oils along with the relative non-biodegradable mineral oils. Petroleum hydrocarbons is the measure of only the mineral oils. Maximum information may be obtained using both methods to measure and characterize oil and grease of all sources.
4. Sampling and Storage
   - 4.1 A representative sample of 1 liter volume should be collected in a glass bottle. Because losses of grease will occur on sampling equipment, the collection of a composite sample is impractical. The entire sample is consumed by this test; no other analyses may be performed using aliquots of the sample.
   - 4.2 A delay between sampling and analysis of greater than 4 hours requires sample preservation by the addition of 5 ml HCl (6.1). A delay of greater than 48 hours also requires refrigeration for sample preservation.
5. Apparatus
   - 5.1 Separatory funnel, 2000 ml, with Teflon stopcock.
   - 5.2 Filter paper, Whatman No. 40, 11 cm.
   - 5.3 Infrared spectrophotometer, scanning or fixed wavelength, for measurement around 2950 cm^{-1}.
   - 5.4 Cells, 10 mm, 50 mm, and 100 mm pathlength, sodium chloride or infrared grade glass.
   - 5.5 Magnetic stirrer, with Teflon coated stirring bars.
6. Reagents
   - 6.1 Hydrochloric acid, 1:1. Mix equal volumes of conc HCl and distilled water.

Issued 1978

7.8 Select appropriate working standards and cell pathlength according to the following table of approximate working ranges:

Pathlength	Range
10 mm	2–40 mg
50 mm	0.5–8 mg
100 mm	0.1–4 mg

Calibrate the instrument for the appropriate cells using a series of working standards (6.5.3). It is not necessary to add silica gel to the standards. Determine absorbance directly for each solution at the absorbance maximum at about 2930 cm^{-1}. Prepare a calibration plot of absorbance vs. mg petroleum hydrocarbons per 100 ml solution.

7.9 After the silica gel has settled in the sample extract, fill a clean cell with solution and determine the absorbance of the extract. If the absorbance exceeds 0.8 prepare an appropriate dilution.

NOTE 2: The possibility that the absorptive capacity of the silica gel has been exceeded can be tested at this point by adding another 3.0 g silica gel to the extract and repeating the treatment and determination.

7.10 Determine the concentration of petroleum hydrocarbons in the extract by comparing the response against the calibration plot.

8. Calculations

8.1 Calculate the petroleum hydrocarbons in the sample using the formula:

$$\text{mg/l Petroleum Hydrocarbons} = \frac{R \times D}{V}$$

where:

R = mg of Petroleum Hydrocarbons as determined from the calibration plot (7.10).
D = extract dilution factor, if used.
V = volume of sample, in liters.

9. Precision and Accuracy

9.1 Precision and accuracy data are not available at this time.

ALKALINITY

Method 310.2 (Colorimetric, Automated, Methyl Orange)

STORET NO. 00410

1. Scope and Application
   - 1.1 This automated method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The applicable range is 10 to 200 mg/1 as $CaCO_3$.
   - 1.2 This method is not an approved NPDES method as cited in the Federal Register December 1, 1976 for samples containing turbidity or color.
2. Summary of Method
   - 2.1 Methyl orange is used as the indicator in this method because its pH range is in the same range as the equivalence point for total alkalinity, and it has a distinct color change that can be easily measured. The methyl orange is dissolved in a weak buffer at a pH of 3.1, just below the equivalence point, so that any addition of alkalinity causes a loss of color directly proportional to the amount of alkalinity.
3. Sample Handling and Preservation
   - 3.1 Sample should be refrigerated at 4°C and run as soon as practical. Do not open sample bottle before analysis.
4. Interferences
   - 4.1 Sample turbidity and color may interfere with this method. Turbidity must be removed by filtration prior to analysis. If sample is filtered, this method is not approved for NPDES monitoring. Sample color that absorbs in the photometric range used will also interfere.
5. Apparatus
   - 5.1 Technicon AutoAnalyzer consisting of:
     - 5.1.1 Sampler I.
     - 5.1.2 Manifold.
     - 5.1.3 Proportioning pump.
     - 5.1.4 Colorimeter equipped with 15 mm tubular flow cell and 550 nm filters.
     - 5.1.5 Recorder equipped with range expander.
6. Reagents
   - 6.1 Methyl Orange: Dissolve 0.125 g of methyl orange in 1 liter of distilled water.
   - 6.2 pH 3.1 Buffer: Dissolve 5.1047 g of potassium acid phthalate in distilled water and add 87.6 ml 0.1 N HCl and dilute to 1 liter. Stable for one week.
   - 6.3 Methyl Orange-Buffered Indicator: Add 1 liter of pH 3.1 buffer (6.2) to 200 ml methyl orange solution (6.1) and mix well. Stable for 24 hours.
   - 6.4 Stock Solution: Dissolve 1.060 g of anhydrous sodium carbonate (oven-dried at 250°C for 4 hours) in distilled water and dilute to 1000 ml. 1.0 ml = 1.00 mg $CaCO_3$.

Approved for NPDES
Issued 1971
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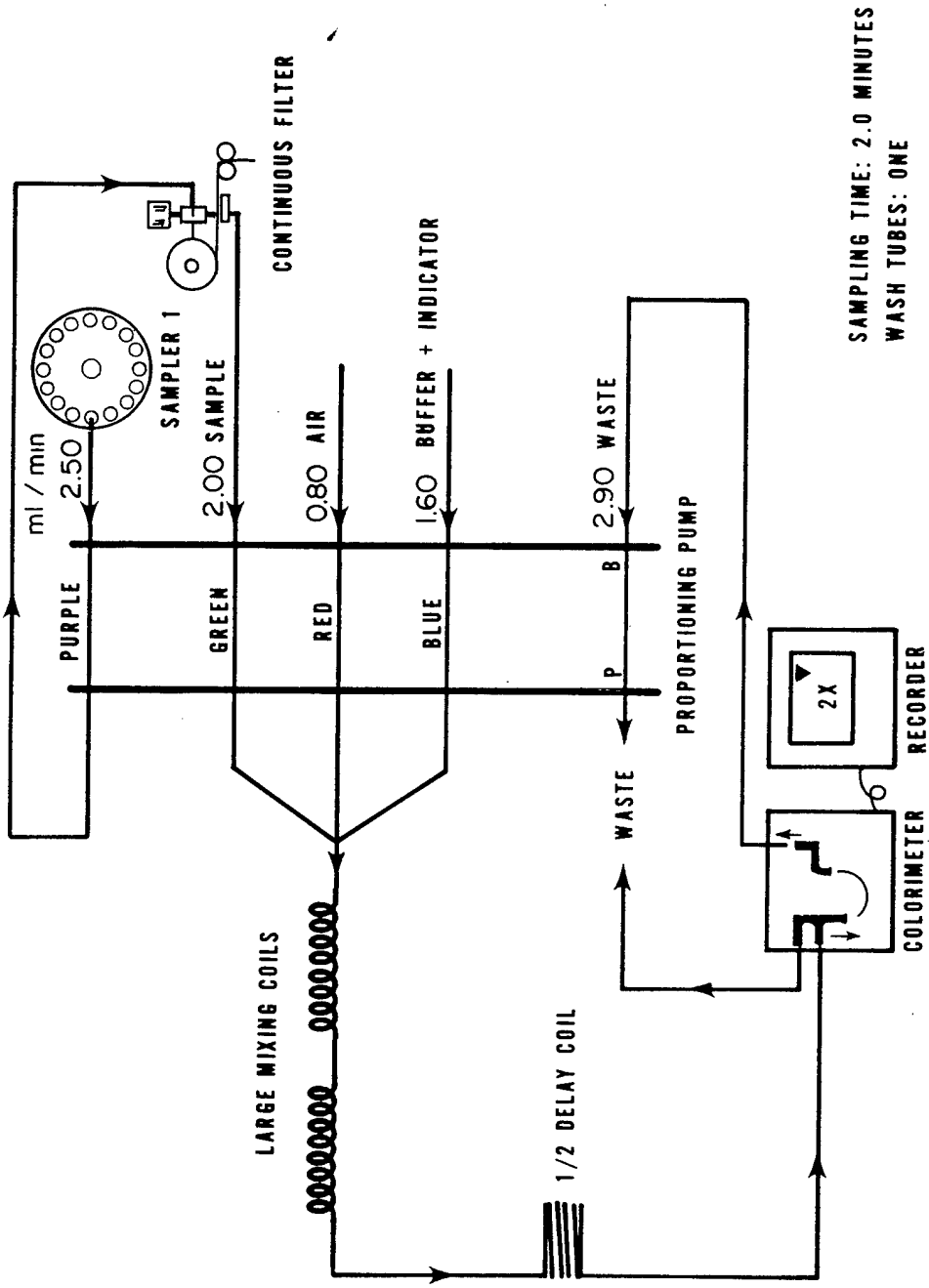

FIGURE 1. ALKALINITY MANIFOLD AA-I

ORGANIC CARBON, TOTAL

Method 415.1 (Combustion or Oxidation)

STORET NO. Total 00680
Dissolved 00681

1. Scope and Application
   1.1 This method includes the measurement of organic carbon in drinking, surface and saline waters, domestic and industrial wastes. Exclusions are noted under Definitions and Interferences.
   1.2 The method is most applicable to measurement of organic carbon above 1 mg/1.
2. Summary of Method
   2.1 Organic carbon in a sample is converted to carbon dioxide (CO_2) by catalytic combustion or wet chemical oxidation. The CO_2 formed can be measured directly by an infrared detector or converted to methane (CH_4) and measured by a flame ionization detector. The amount of CO_2 or CH_4 is directly proportional to the concentration of carbonaceous material in the sample.
3. Definitions
   3.1 The carbonaceous analyzer measures all of the carbon in a sample. Because of various properties of carbon-containing compounds in liquid samples, preliminary treatment of the sample prior to analysis dictates the definition of the carbon as it is measured. Forms of carbon that are measured by the method are:
      A) soluble, nonvolatile organic carbon; for instance, natural sugars.
      B) soluble, volatile organic carbon; for instance, mercaptans.
      C) insoluble, partially volatile carbon; for instance, oils.
      D) insoluble, particulate carbonaceous materials, for instance; cellulose fibers.
      E) soluble or insoluble carbonaceous materials adsorbed or entrapped on insoluble inorganic suspended matter; for instance, oily matter adsorbed on silt particles.
   3.2 The final usefulness of the carbon measurement is in assessing the potential oxygen-demanding load of organic material on a receiving stream. This statement applies whether the carbon measurement is made on a sewage plant effluent, industrial waste, or on water taken directly from the stream. In this light, carbonate and bicarbonate carbon are not a part of the oxygen demand in the stream and therefore should be discounted in the final calculation or removed prior to analysis. The manner of preliminary treatment of the sample and instrument settings defines the types of carbon which are measured. Instrument manufacturer's instructions should be followed.

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7.5 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to step 7.3.

NOTE 3: This standard is not required by some instruments.

7.6 Blank solution: Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.

8. Procedure

8.1 Follow instrument manufacturer's instructions for calibration, procedure, and calculations.

8.2 For calibration of the instrument, it is recommended that a series of standards encompassing the expected concentration range of the samples be used.

9. Precision and Accuracy

9.1 Twenty-eight analysts in twenty-one laboratories analyzed distilled water solutions containing exact increments of oxidizable organic compounds, with the following results:

Increment as TOC mg/liter	Precision as Standard Deviation TOC, mg/liter	Accuracy as Bias, %	Accuracy as Bias, mg/liter
4.9	3.93	+15.27	+0.75
107	8.32	+ 1.01	+1.08

(FWPCA Method Study 3, Demand Analyses)

Bibliography

1. Annual Book of ASTM Standards, Part 31, "Water", Standard D 2574–79, p 469 (1976).
2. Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 532, Method 505, (1975).

FORMULA: various

M.W.: various

ASBESTOS (bulk)

METHOD: 9002
ISSUED: 5/15/89

EPA Standard (Bulk): 1%

PROPERTIES: solid, fibrous, crystalline, anisotropic

SYNONYMS: actinolite [CAS #13768-00-8], or ferroactinolite; cummingtonite-grunerite (amosite) [CAS #12172-73-5]; anthophyllite [CAS #17068-78-9]; chrysotile [CAS #12001-29-5] or serpentine; crocidolite [CAS #12001-28-4] or riebeckite; tremolite [CAS #14567-73-8]; amphibole asbestos.

SAMPLING

BULK SAMPLE: 1 to 10 grams

SHIPMENT: seal securely to prevent escape of asbestos

SAMPLE STABILITY: stable

BLANKS: none required

ACCURACY

RANGE STUDIED: <1% to 100% asbestos

BIAS: not determined

PRECISION: not determined

MEASUREMENT

TECHNIQUE: MICROSCOPY, STEREO AND POLARIZED LIGHT, WITH DISPERSION STAINING

ANALYTE: actinolite asbestos, amosite, anthophyllite asbestos, chrysotile, crocidolite, tremolite asbestos

EQUIPMENT: microscope, polarized light: 100–400X dispersion staining objective, stereo microscope: 10–45X

RANGE: 1% to 100% asbestos

ESTIMATED LOD: <1% asbestos [1]

PRECISION: not determined

APPLICABILITY: This method is useful for the qualitative identification of asbestos and the semi-quantitative determination of asbestos content of bulk samples, expressed as a percent of projected area. The method measures percent asbestos as perceived by the analyst in comparison to standard area projections, photos, and drawings, or trained experience. The method is not applicable to samples containing large amounts of fine fibers below the resolution of the light microscope.

INTERFERENCES: Other fibers with optical properties similar to the asbestos minerals may give positive interferences. Optical properties of asbestos may be obscured by coating on the fibers. Fibers finer than the resolving power of the microscope (ca. 0.3 µm) will not be detected. Heat and acid treatment may alter the index of refraction of asbestos and change its color.

OTHER METHODS: This method (originally designated as method 7403) is designed for use with NIOSH Methods 7400 (phase contrast microscopy) and 7402 (electron microscopy/EDS). The method is similar to the EPA bulk asbestos method [1].

5. In a hood, open sample container and with tweezers remove small, representative portions of the sample.
   a. If there are obvious separable layers, sample and analyze each layer separately.
   b. If the sample appears to be slightly inhomogeneous, mix it in the sample container with tweezers or a spatula before taking the portion for analysis. Alternatively, take small representative portions of each type of material and place on a glass slide.
   c. On hard tiles that may have thin, inseparable layers, use a scalpel to cut through all the layers for a representative sample. Then cut it into smaller pieces after placing RI liquid on it before trying to reduce the thickness. Alternatively, use a low-speed hand drill equipped with a burr bit to remove material from hard tiles. Avoid excessive heating of the sample which may alter the optical properties of the material.
   NOTE: This type of sample ofter requires ashing or other specialized preparation.
   d. If the sample has large, hard particles, grind it in a mortar. Do not grind so fine that fiber characteristics are destroyed.
   e. If necessary, treat a portion of the sample in a hood with an appropriate solvent to remove binders, tars, and other interfering materials which may be present in the sample. Make corrections for the non-asbestos material removed by this process.
   NOTE: Other methods of sample preparation such as acid and sodium metaphosphate treatment and ashing are not normally necessary. However, if needed, use as described in Reference [1].
6. After placing a few drops of RI liquid on the slide, put a small portion of sample in the liquid. Tease apart with a needle or smash small clumps with the flat end of a spatula or probe, producing a uniform thickness of particles so that better estimates of projected area percentages can be made. Mix the fibers and particles on the slide so that they are as homogeneous as possible.
   NOTE: An even dispersion of sample should cover the entire area under the cover slip. Some practice will be necessary to judge the right amount of material to place on the slide. Too little sample may not give sufficient information and too much sample cannot be easily analyzed.

CALIBRATION AND QUALITY CONTROL:

7. Check for contamination of microscope slides, cover slips and refractive index liquids once per day of operation. Record results in a separate logbook.
8. Verify the refractive indices of the refractive index liquids used once per week of operation. Record these checks in a separate logbook.
9. Follow the manufacturer's instructions for illumination, condenser alignment and other microscope adjustments. Perform these adjustments prior to each sample set.
10. Determine precent of each identified asbestos species by comparision to standard projections (Figure 1) [1]. If no fibers are detected in a homogeneous sample, examine at least two additional preparations before concluding that no asbestos is present.
11. If it appears that the preparation technique might not be able to produce a homogeneous or representative sample on the slide, prepare a duplicate slide and average the results. Occasionally, when the duplicate results vary greatly, it will be necessary to prepare additional replicate slides and average all the replicate results. Prepare duplicate slides of at least 10% of the samples analyzed. Average the results for reporting.
12. Analyze about 5% blind samples of known asbestos content.
13. Laboratories performing this analytical method should participate in the National Voluntary Labortory Accreditation Program [5] or a similar interlaboratory quality control program. Each analyst should have completed formal training in polarized light microscopy and its application to crystalline materials. In lieu of formal training, laboratory training in asbestos bulk analysis under the direction of a trained asbestos bulk analyst may be substituted. Due to the subjective nature of the method, frequent practice is essential in order to remain proficient in estimating projected area percentages.

h. Identification of amosite. Prepare a slide in 1.680 RI liquid. Observe the fiber morphology for amosite characteristics: straight fibers and fiber bundles with broom-like or splayed ends. If the morphology matches amosite, examine the fibers using the dispersion staining objective. Blue and pale blue colors indicate the cummingtonite form of amosite, and gold and blue colors indicate the grunerite form of amosite. If amosite is confirmed by this test, go to step 15 for quantitative estimation, otherwise continue.

i. Identification of anthophyllite-tremolite-actinolite. Prepare a slide in 1.605 HD RI liquid. Examine morphology for comparision to anthophyllite-tremolite-actinolite asbestos. The refractive indices for these forms of asbestos vary naturally within the species. Anthophyllite can be distinguished from actinolite and tremolite by its nearly parallel extinction. Actinolite has a light to dark green color under plane-polarized light and exhibits some pleochroism. For all three, fibers will be straight, single fibers possibly with some larger composite fibers. Cleavage fragments may also be present. Examine using the central stop dispersion staining objective. Anthophyllite will exhibit central stop colors of blue and gold/gold-magenta; tremolite will exhibit pale blue and yellow; and actinolite will exhibit magenta and golden-yellow colors.

NOTE: In this refractive index range, wollastonite is a common interfering mineral with similiar morphology including the presence of cleavage fragments. It has both positive and negative sign of elongation, parallel extinction, and central stop dispersion staining colors of pale yellow and pale yellow to magenta. If further confirmation of wollastonite versus anthophyllite is needed, go to step "j". If any of the above forms of asbestos was confirmed above, go to step 15 for quantitative estimation. If none of the tests above confirmed asbestos fibers, examine the additional preparations and if the same result occurs, report the absence of asbestos in this sample.

j. Wash a small portion of the sample in a drop of concentrated hydrochloric acid on a slide. Place the slide, with cover slip in place, on a warm hot plate until dry. By capillary action, place 1.620 RI liquid under the cover slip and examine the slide. Wollastonite fibers will have a "cross-hatched" appearance across the length of the fibers and will not show central stop dispersion colors. Anthophyllite and tremolite will still show their original dispersion colors.

NOTE: There are alternative analysis procedures to the step-wise approach outlined above which will yield equivalent results. Some of these alternatives are:

i. Perform the initial scan for the presence of asbestos using crossed polars as well as the first-order red compensator. This allows for simultaneous viewing of birefringent and amorphous materials as well as determining their sign of elongation. Some fibers which are covered with mortar may best be observed using this configuration.

ii. Some analysts prefer to mount their first preparation in a RI liquid different than any asbestos materials and conduct their initial examination under plane-polarized light.

iii. If alternative RI liquids are used from those specified, dispersion staining colors observed will also change. Refer to an appropriate reference for the specific colors associated with asbestos in the RI liquids actually used.

QUANTITATIVE ASSESSMENT:

15. Estimate the content of the asbestos type present in the sample using the 1.550 RI preparation. Express the estimate as an area percent of all material present, taking into account the loading and distribution of all sample material on the slide. Use Figure 1 as an aid in arriving at your estimate. If additional unidentified fibers are present in the sample, continue with the qualitative measurement (step 14).

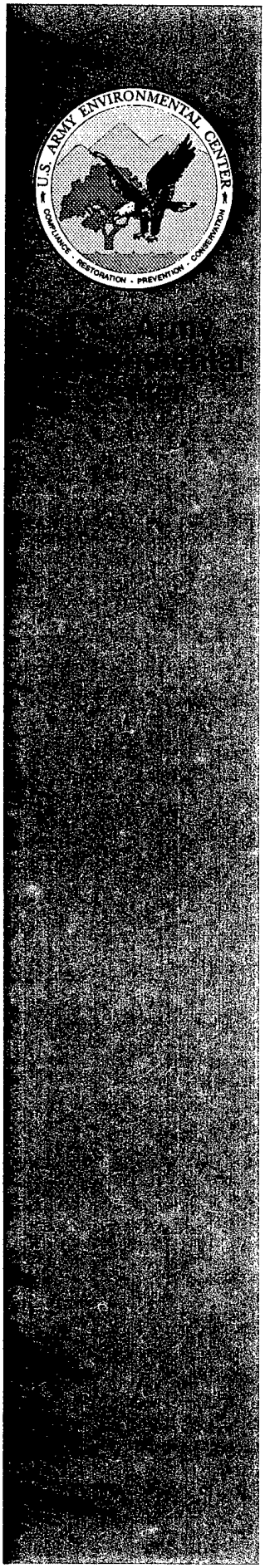
NOTE: Point-counting techniques to determine percentages of the asbestos minerals are not generally recommended. The point-counting method only produces accurate quantitative

Figure 1. Percent estimate comparator.

Table 1. Optical Properties of Asbestos Fibers (Continued)

Mineral	Extinction	Sign of Elongation	Central Stop Dispersion Staining Colors: RI Liquid	⊥ to Vibration	∥ to Vibration
Chrysotile	Parallel to fiber length	+ (length slow)	1.550 HD	Blue	Blue–magenta
Cummingtonite–Grunerite (Amosite)	Parallel to fiber length	+ (length slow)	1.670	Red magenta to blue	Yellow
			Fibers subjected to high temperatures will not dispersion-stain.		
Cummingtonite			1.680	pale blue	blue
Grunerite			1.680	blue	gold
Crocidolite (Riebeckite)	Parallel to fiber length	– (length fast)	1.700	Red magenta	Blue–magenta
			1.680	yellow	pale yellow
Anthophyllite	Parallel to fiber length	+ (length slow)	1.605 HD	Blue	Gold to gold–magenta
			1.620 HD	Blue–green	Golden–yellow
Tremolite–Actinolite	Oblique – 10 to 20° for fragments. Some composite fibers show ∥ extinction.	+ (length slow)	1.605 HD	Pale blue (tremolite)	Yellow (tremolite)
				Yellow (actinolite)	Pale yellow (actinolite)

HD = high-dispersion RI liquid series.



Quality Assurance Project Plan

Supplement A

Main Post Site Investigation (SI)
Fort Devens, Massachusetts

Submitted to

U.S. Army Environmental Center (USAEC)
Formerly USATHAMA
Aberdeen Proving Ground, Maryland

Revision 2
August 1994

Arthur D. Little, Inc.
Acorn Park
Cambridge, Massachusetts
02140-2390

ADL Reference 67064-14

DAAA15-91-D-0016
Delivery Order 0004

AEC Form 45, 1 Feb 93 replaces THAMA Form 45 which is obsolete.

Quality Assurance Project Plan

Supplement A

Arthur D Little

Main Post Site Investigation (SI) Fort Devens, Massachusetts

Program Manager, Robert Lambe — Date: 8-16-94

Task Manager, Mark Heuberger — Date: 8/16/94

Program Quality Assurance Officer, Stuart Canton — Date: 8-17-94

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List of Acronyms and Abbreviations

See Quality Assurance Project Plan.

1.0 Project Description

1.1 Introduction

This Supplement to the Quality Assurance Project Plan (QAPjP) for Fort Devens, Massachusetts, has been prepared to address task-specific activities associated with the Main Post Supplemental Site Investigation (SI) and Remedial Investigation/ Feasibility Study (RI/FS) (Modification 2 to Task 0004).

The overall Quality Assurance/Quality Control (QA/QC) activities for all Arthur D. Little activities at Fort Devens are contained in the Final QAPjP for Fort Devens, Massachusetts, dated June 16, 1993. Supplements to the QAPjP address task-specific activities. Specifically, this supplement follows the same organizational format as the QAPjP and provides additional information in Section 1.3, Task Objectives and Scope of Work; Section 2.0, Project and QA/QC Organization and Responsibilities; Section 3.2, QA Objectives for Fort Devens Data; Section 4.2, Field QC Samples; Section 4.4, Sampling Equipment and Procedures; Section 5.1, Field Custody Procedures for new activities or procedures for the specific tasks; Section 7.4, Analytical Methods; and Section 7.5, Field Analytical methods. Reference is made to the Final QAPjP for all other QA/QC activities and procedures.

1.2 Site Background

1.2.1 Site Description
See Quality Assurance Project Plan.

1.2.2 Site History
See Quality Assurance Project Plan.

1.2.3 Previous Investigations
See Quality Assurance Project Plan.

1.3 Task Objectives and Scope of Work

1.3.1 Main Post SI
The primary objectives of the Fort Devens Main Post SI are as follows:

- To conduct an SI at 11 study areas (SAs) at Fort Devens to assess the presence of environmental contamination.

- To evaluate the SI data to determine which sites:
  - Require no further action
  - Are candidates for removal action
  - Require inclusion in an RI/FS
- To rank in order of priority those sites recommended for an RI/FS, based upon their actual or potential threat to human health or the environment
- To conduct the Main Post section of the Nashua River Study

The SI will be conducted at the following study areas at the Main Post of Fort Devens:

Group	Study Area Number	Site Name
4	33	DEH Entomology Shop (Building 262)
	34	Former DEH Entomology Shop (Building 245)
	35	Former DEH Entomology Shop (Building 254)
	36	Former DEH Entomology Shop (Building 2728)
	37	Golf Course Entomology Shop (Building 3622)
8	16	Shoppette Debris Disposal Area
	17	Little Mirror Lake
	29	Transformer Storage Area
	39	Transformer near Building 4250 (Sylvania Building)
9	10	Construction Debris Area
	11	Construction Debris Area
--	--	Nashua River Study

Figure 1-1A indicates the locations of the study areas within Fort Devens.

The Work Breakdown Structure for the Fort Devens Main Post SI is presented in Figure 1-2A. The individual subtasks to complete this task order are described in detail in the Supplemental Work Plan.

The sampling objectives, sampling location and frequency, and sample designation for field investigations at each study area are presented in detail in the Supplemental Work Plan.

1.3.2 Main Post SSI and RI/FS

Site Investigations were conducted by Arthur D. Little at 13 study areas as part of the Main Post SI. The background, investigation results, preliminary risk evaluation, and

conclusions and recommendations for each SA are described in the Main Post Site Investigation Report. Supplemental SIs have been recommended at four SAs: SA-17, Mirror Lake and Little Mirror Lake; SA-39, Sylvania Building Site; SA-51, O'Neill Building Site; and Building 3606 at SA-37, Golf Course Entomology Shops. An RI/FS has been recommended for SA-11, Construction Debris Area, which has been designated as Area of Concern (AOC) 11. The primary objectives of the Fort Devens Main Post SSI are as follows:

- To conduct Supplemental Site Investigations at four SAs to assess the presence of environmental contamination

- To evaluate the SSI data to determine which sites:
  - Require no further action
  - Are candidates for removal action
  - Require inclusion in an RI/FS

The primary objectives of the RI/FS for AOC-11 are as follows:

- The objective of the RI at AOC-11 is to provide data regarding the physical characteristics of the area, the nature and extent of contamination, and contaminant fate and transport. The RI will also provide data necessary to complete the Baseline Human Health and Ecological Risk Assessments and the Feasibility Study.

- The objectives of the Baseline Risk Assessment (BRA) are to assess and quantify the potential human health and ecological risks resulting from site-derived contaminants in all media, and to identify those areas requiring remediation.

- The objective of the FS is to develop and evaluate a range of remedial alternatives to address areas of contamination. The alternatives that are developed will be effective for all contaminants and media of interest. The FS will also provide a comparative analysis of alternatives with respect to nine criteria as required under CERCLA.

The Work Breakdown Structure for the Fort Devens Main Post Supplemental SI and RI/FS is presented in Figure 1-2A. The individual subtasks to complete this task order are described in detail in the Supplemental Work Plan.

The Supplemental SI and RI field investigations will include the tasks listed below.

- Unexploded ordnance (UXO) clearance, as appropriate
- Wetland delineation and assessment
- Location and elevation survey

- Surveys for metal objects
- Test pit excavation
- Soil borings and subsurface soil sampling
- Installation of ground water monitoring well
- Monitoring well development
- Ground water sampling
- Geoprobe® ground water and soil sampling
- Surface water and sediment sampling
- Ground water and surface water level measurement
- Ambient air and particulate sampling
- Radiation survey where appropriate

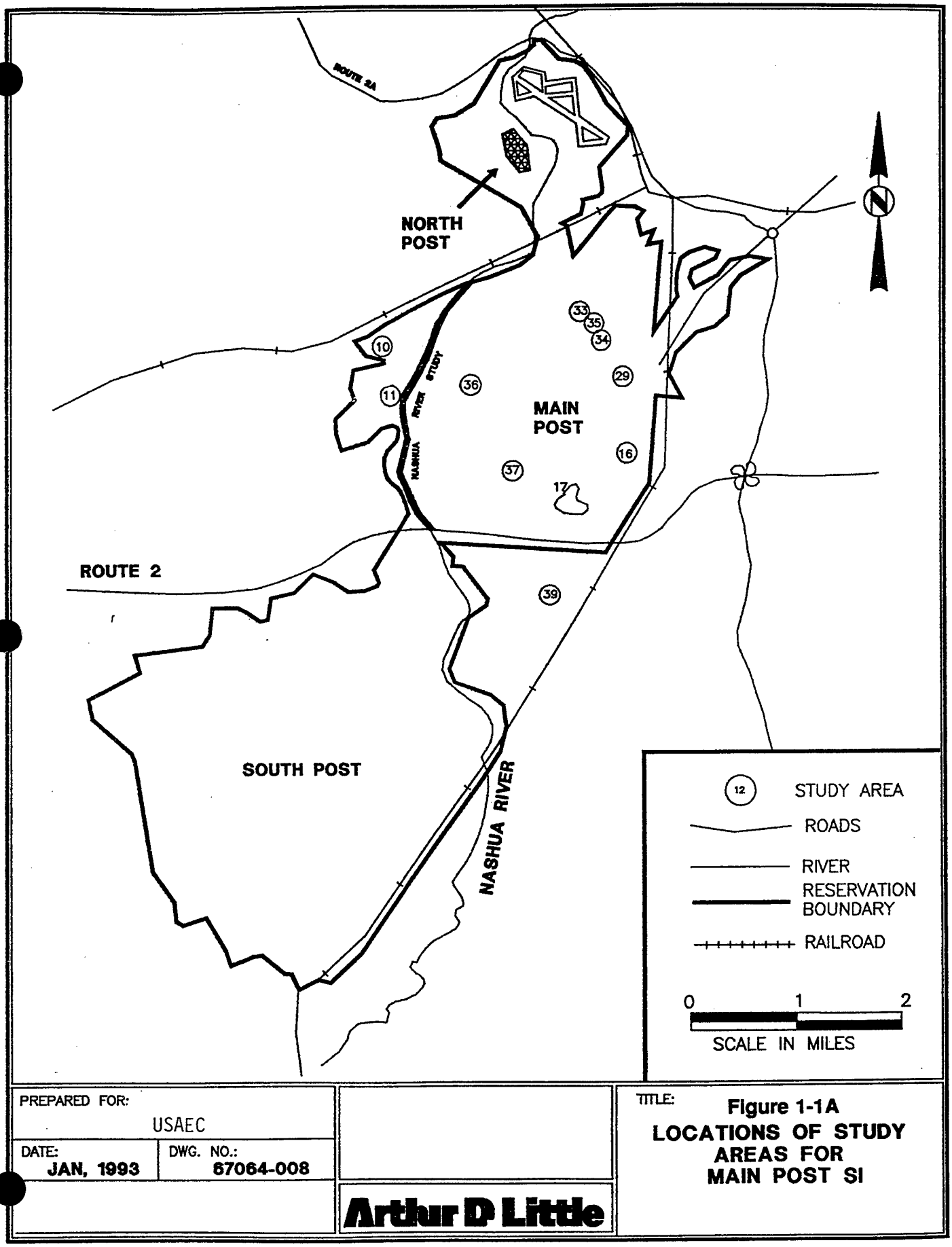
The sampling objectives, sampling location and frequency, and sample designation for field investigations at each study area are presented in detail in the Supplemental Work Plan. Table 4-2A shows sampling type and frequencies.

1.4 Applicability

See Quality Assurance Project Plan.

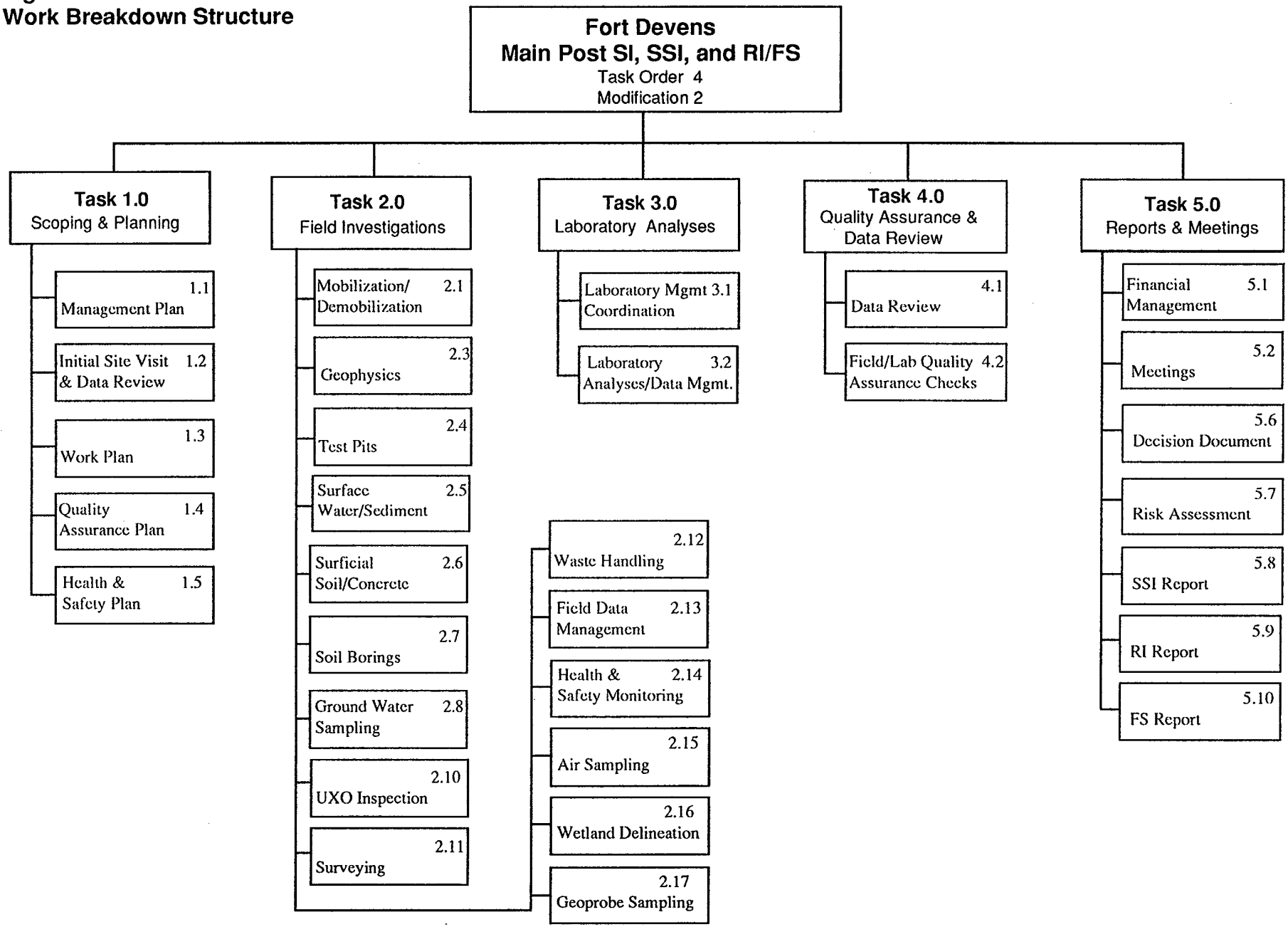
1.5 Organization of Document

See Quality Assurance Project Plan.



PREPARED FOR: USAEC		TITLE: **Figure 1-1A LOCATIONS OF STUDY AREAS FOR MAIN POST SI**
DATE: **JAN, 1993** / DWG. NO.: **67064-008**		
	Arthur D Little	

Figure 1-2A
Work Breakdown Structure



2.0 Project and QA/QC Organization and Responsibilities

The organizational structure for the Fort Devens SI is presented in Figure 2-1A.

2.1 Project Organization

2.1.1 Program Manager
See Quality Assurance Project Plan.

2.1.2 Task Manager
Mr. Mark Heuberger is the Arthur D. Little Task Manager for Delivery Order 0004 and will work directly with Dr. Lambe. As Task Manager, his responsibilities include: project staffing and direct management of all staff assigned to Delivery Order 0004; direct financial and schedule control; review and approval of all deliverables; recommending corrective actions, if necessary, to the Program Manager; and maintaining a liaison with the USAEC Project Officer and Fort Devens Environmental Office Manager. In this role, the Task Manager will be responsible for ensuring that the USAEC Project Officer and Fort Devens Environmental Office Manager are kept informed of all technical progress as necessary.

2.1.3 Task Staff
Subtask Managers are assigned to specific Delivery Orders as required by the scope of work. Subtask Managers assigned to this Delivery Order are:

- Field Investigation and Deputy Task Manager - Erin Healy
- Laboratory Analysis and QA/Data Review - Hilton Rivera

2.2 Arthur D. Little QA/QC Organization

See Quality Assurance Project Plan.

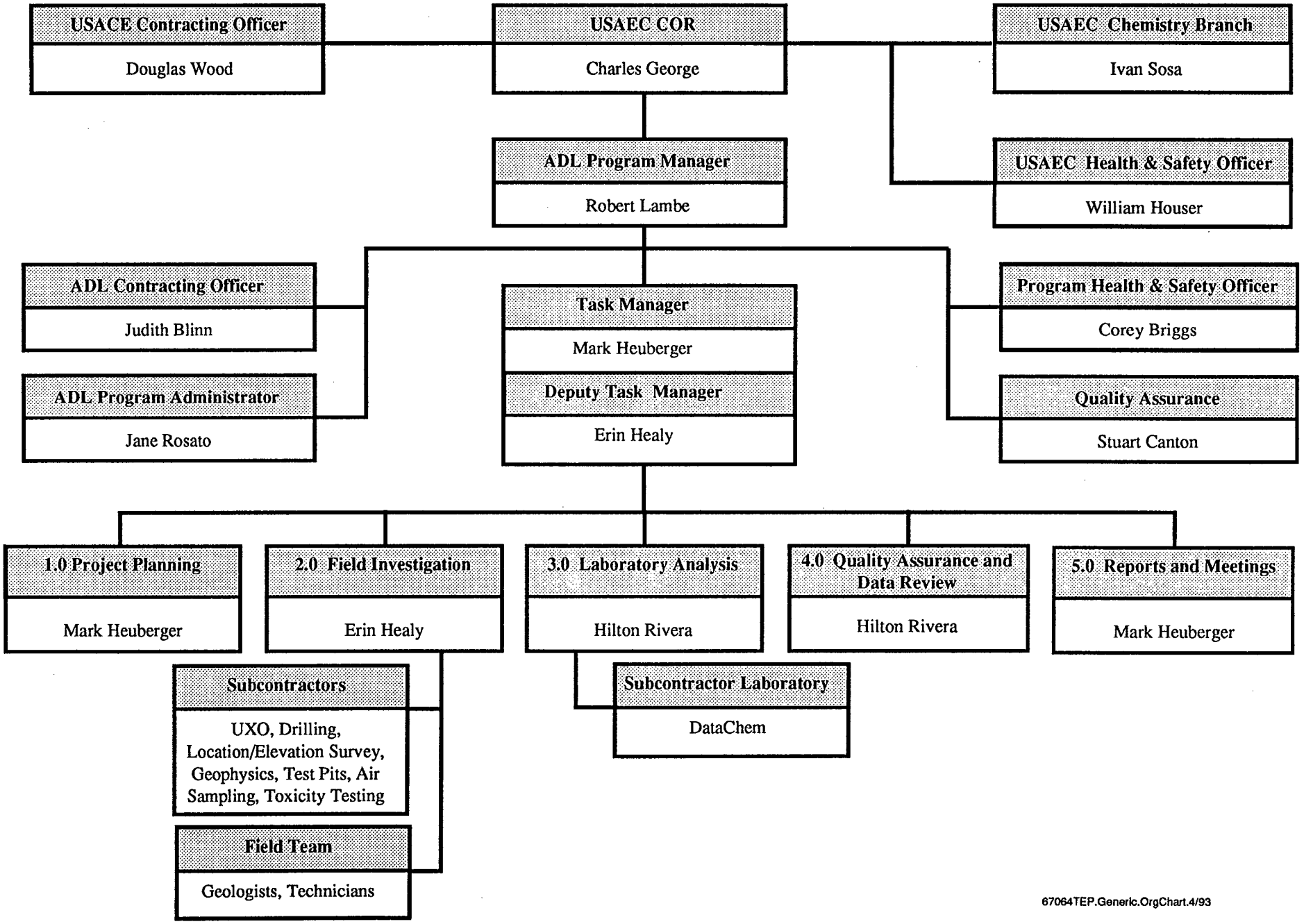
2.2.1 Program QA Officer
See Quality Assurance Project Plan.

2.2.2 Lead Chemist
See Quality Assurance Project Plan.

2.3 DataChem Project QA/QC Organization

See Quality Assurance Project Plan.

Figure 2-1A
Fort Devens Main Post SSI and RI/FS — Organizational Chart



3.0 QA Objectives for Measurement Data in Terms of Precision, Accuracy, Representativeness, Completeness, Comparability

3.1 Introduction

See Quality Assurance Project Plan.

3.2 QA Objectives for Fort Devens Data

See Quality Assurance Project Plan.

A non-USAEC performance demonstrated laboratory will be used to perform some selected field screening analyses. The purpose of these analyses will be to determine whether additional analysis by a USAEC-performance demonstrated laboratory is appropriate. The quality of the field screening data generated by the non-USAEC-performance demonstrated laboratory will be comparable to EPA Level III data quality (see QAPjP).

3.2.1 Precision
See Quality Assurance Project Plan.

3.2.2 Accuracy
See Quality Assurance Project Plan.

3.2.3 Representativeness
See Quality Assurance Project Plan.

3.2.4 Completeness
See Quality Assurance Project Plan.

3.2.5 Comparability
See Quality Assurance Project Plan.

4.0 Sample Collection

4.1 Sample Containers, Preservation, and Handling

4.1.1 Sample Containers
See Quality Assurance Project Plan.

4.1.2 Sample Preservation and Holding Times
See Quality Assurance Project Plan.

4.2 Field QC Samples

See Quality Assurance Project Plan.

4.2.1 Main Post SI
Table 4-1A provides a summary of field QC samples to be collected during the Main Post SI. The types and frequency of field QC samples to be collected as part of the Main Post SI are presented in Table 4-2A.

4.2.2 Main Post SSI and RI/FS
The types and frequency of field QC samples for the SSI and RI/FS is summarized in Table 4-2A. The analytical program for field and QC samples is summarized for aqueous, soil, and air matrices in Tables 4-3A, 4-4A, and 4-5A.

4.3 Sample Handling

See Quality Assurance Project Plan.

4.4 Sampling Equipment and Procedures

4.4.1 Test Pit Sampling Procedures
See Quality Assurance Project Plan.

4.4.2 Surface Water Sampling Procedures
See Quality Assurance Project Plan.

4.4.3 Sediment Sampling Procedures
See Quality Assurance Project Plan.

Table 4-1A: Summary of Field Quality Control Samples

	TCL-VOC	TCL-BNA	TCL-PCB/PEST (Chlorinated)	TAL-Metals	Nitrate	TPHC	Water Quality Parameters	Explosives
AQUEOUS								
Field Duplicates	2	2	2	3	2	2	2	2
MS/MSD	4	4	4	4	4	0	4	4
Field Blanks	4	4	4	4	4	4	4	4
Rinsate Blanks	25	25	25	25	25	25	25	25
Trip Blanks	16	0	0	0	0	0	0	0
NON-AQUEOUS								
Field Duplicates	12	12	6	12	6	6	0	4
MS/MSD	24	24	12	24	12	12	0	8
Field Blanks	12	12	6	12	6	6	0	4
Rinsate Blanks	24	24	12	24	12	12	0	8
Trip Blanks	29	0	0	0	0	0	0	0

Table 4-2A: Frequency of Field Quality Control Samples

Field Blank:	One per 20 samples or 5%, whichever is greater[a]; ASTM Type I deionized water or equivalent used for organic field blanks; distilled, deionized water used for inorganic field blanks.
Equipment/ Rinsate Blank:	One per day per equipment type; ASTM Type I deionized water or equivalent used for organic rinsate blanks; distilled, deionized water used for inorganic rinsate blanks.
Trip Blank:	For volatile organic analyses; minimum is one per cooler containing any samples for volatile organic analyses. Purged deionized ASTM Type I deionized water or equivalent is to be used for trip blanks.
Field Duplicate:	One per 20 samples or 5%[a] per matrix.
Matrix Spike/ Matrix Spike Duplicate:	Organic analysis only: one set per matrix per area, but no more than one set per 20 samples or 5%[a]; actual field sample must be used.[b]
Matrix Spike/ Lab Duplicate:	Inorganic analysis only; one set per matrix per area, but no more than one set per 20 samples; actual field sample must be used.

a = When a group of less than 20 samples is collected during a sampling event, blanks, duplicates, and MS/MSD samples need to be collected, resulting in a higher percentage of QA/QC samples than indicated above.

b = Additional sample volume may be required.

Table 4-3A: Analytical Program Summary - Aqueous Matrix

PARAMETER	FIELD SAMPLES	FIELD DUPLICATE	MATRIX SPIKE	MATRIX SPIKE DUPLICATE	FIELD BLANK	RINSATE BLANK	TRIP BLANK	TOTAL SAMPLES
TCL VOA	33	2	2	2	4	25	16	84
TCL SVOA	33	2	2	2	4	25	0	68
TCL PEST/PCB	36	2	2	2	4	25	0	71
TAL METALS	55	3	3	3	4	25	0	93
TPH-IR	29	2	0	0	4	25	0	60
ALKALINITY	29	2	0	0	4	25	0	60
ANIONS (Cl,SO_4)	42	2	2	2	4	25	0	77
HARDNESS	29	2	2	2	4	25	0	64
NITRATE/ NITRITE	29	2	2	2	4	25	0	64
TKN	29	2	2	2	4	25	0	64
TSS	39	2	0	0	4	25	0	70
T-PHOSPHORUS	29	2	2	2	4	25	0	64
TDS	10	1	0	0	4	25	0	40
EXPLOSIVES	19	2	2	2	4	25	0	54

Table 4-4A: Analytical Program Summary - Soil Matrix

PARAMETER	FIELD SAMPLES	FIELD DUPLICATE	MATRIX SPIKE	MATRIX SPIKE DUPLICATE	FIELD BLANK	RINSATE BLANK	TRIP BLANK	TOTAL SAMPLES
TCL VOA	74	4	4	4	4	25	16	131
TCL SVOA	74	4	4	4	4	25	0	115
TCL PEST/PCB	74	4	4	4	4	25	0	115
TCL PCB	5	1	0	0	0	25	0	31
TAL METALS	80	4	4	4	4	25	0	121
TPH-IR	65	3	0	0	4	25	0	97
TOC	39	2	0	0	4	25	0	70
GRAIN SIZE	39	0	0	0	0	25	0	39
EXPLOSIVES	19	1	1	1	4	25	0	51

Table 4-5A: Analytical Program Summary - Air Matrix

PARAMETER	FIELD SAMPLES	FIELD DUPLICATE	PROCESS BLANK	TRIP/FIELD BLANKS	TOTAL SAMPLES
TO-14 VOCs	4	2	2	2	**10**
TO-4 PCBs	4	2	2	2	**10**
PM-10 Metals	4	2	2	2	**10**

4.4.4 Surface Soil Sampling Procedures
See Quality Assurance Project Plan.

4.4.5 Concrete/Asphalt Chip Sampling Procedures
See Quality Assurance Project Plan.

4.4.6 Soil Boring Procedures
See Quality Assurance Project Plan.

4.4.6.1 Subsurface Clearance Program. See Quality Assurance Project Plan.

4.4.7 Ground Water Sampling Procedures
See Quality Assurance Project Plan.

4.4.8 Wipe Sampling Procedures
See Quality Assurance Project Plan.

4.4.9 Sample Location and Elevation Survey Procedures
See Quality Assurance Project Plan.

4.4.10 Investigation-Derived Waste Handling Procedures
See Quality Assurance Project Plan.

4.4.11 Geoprobe® Sampling Procedures
See Quality Assurance Project Plan.

4.4.12 Ambient Air Sampling Procedures
Air quality samples will be collected according to the Quality Assurance/Quality Control Plan of our selected subcontractor. Activities related to the sampling are outlined as follows:

- A temporary, transportable meteorological monitoring station will be installed in accordance with the criteria set forth in *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV-Meteorological Measurements* (EPA, 1989).

- The meteorological monitoring station will record temperature, relative humidity, wind speed, wind direction, and barometric data during regularly established intervals before and during sampling events.

- Metals samples will be collected over a 24-hour period using high volume samplers, and will be analyzed for TAL metals by ICP. Sampling and analysis will be completed in accordance with *Standard Operating Procedures for the ICP-DES Determination of Trace Elements in Suspended Particulate Matter Collected*

on glass-Fiber Filters (EPA, 1983). PM-10 samples will be collected in accordance with 40 CFR 50 Appendix J.

- PCB samples will be collected and analyzed in accordance with EPA Method TO-4, as described in *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (EPA document 600/4-89-017). Samples will be collected over a 24-hour period. Detection limits of less than one nanogram per cubic meter are required.

- VOC samples will be collected in SUMMA polished stainless steel canisters in accordance with EPA Method TO-14, as described in *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (EPA Document 600/4-84-041). VOC samples will be collected over an 8-hour period.

One set of trip/field blanks, one set of process blanks, and one set of field duplicates will be analyzed with each sampling round.

4.4.13 Sediment and Surface Water Bioassays (Toxicity Testing)

Aquatic toxicity testing will be conducted as part of the RI in accordance with the Quality Assurance/Quality Control Plan provided by our selected subcontractor. The following minimum testing will be performed:

- Surface water toxicity tests will be conducted for the appropriate time and using the appropriate species. If acute toxicity is suspected, definitive tests will be conducted according to current EPA short-term methods for estimating chronic toxicity of effluent and receiving waters to freshwater organisms.

- Sediment toxicity tests will be conducted for the appropriate time and using the appropriate species. The definitive tests will be conducted only with full-strength sediment samples. The test will be conducted according to current EPA or ASTM sediment testing methods for freshwater organisms.

- Sediment elutriate toxicity tests will be conducted for the appropriate times and using the appropriate species. After screening, if no acute toxicity is detected, the definitive tests will be conducted only with full-strength elutriate samples to verify the lack of chronic toxicity. If toxicity is suspected, the definitive tests will be conducted with five concentrations of elutriate that bracket the anticipated no observed effect concentration. The definitive tests will be conducted according to current EPA methods.

5.0 Sample Custody

5.1 Field Custody Procedures

See Quality Assurance Project Plan.

5.1.1 Main Post SI

Figure 5-1A summarizes the site identification and field numbering system to be applied to all samples collected during completion of the Main Post SI.

5.1.2 Main Post SSI and RI/FS

Figure 5-2A summarizes the site identification and field numbering system to be applied to all samples collected during completion of the Main Post SSI and RI/FS.

5.2 Laboratory Custody Procedures

See Quality Assurance Project Plan.

Figure 5-1A: Site Identification and Field Sample Numbering System
Fort Devens Main Post Site Investigation
Fort Devens, Massachusetts

SITE IDENTIFICATION CODE (10 Characters)									
CHARACTER NUMBER									
1	2	3	4	5	6	7	8	9	10
Study Area Number: SA No.: 33, 34, 35, 36, 37, 16, 17, 29, 39, 10, 11, Nashua River (NR)		Site Type: S = Surface soil B = Soil boring M = Monitoring well W = Surface water D = Sediment P = Wipe C = Concrete chip A = Asphalt	Hyphen	Year of activity		Hyphen	Location number: The number of the boring, surface soil, monitoring well, etc. sampling location		Shallow to deep designator for monitoring well clusters (A-D)

QC SAMPLE IDENTIFICATION CODE (8 CHARACTERS)							
CHARACTER NUMBER							
1	2	3	4	5	6	7	8
Event Code: A = Early Spring 1993	Study Area Code: A = 33 B = 34 C = 35 D = 36 E = 37 F = 16 G = 17 H = 29 I = 39 J = 10 K = 11 L = NR	QC Sample Type: T = Trip Blank D = Duplicate F = Field Blank R = Rinsate Blank X = Field Sample	Sampling Technique/Media Type: SS = Surface Soil EB = Subsurface Soil MW = Groundwater TP = Test Pit (Soil) SD = Sediment SW = Surface Water WP = Wipe CP = Concrete Chip AS = Asphalt		Sampling Location Number: 01 thru 99		Sample Location/ Analyte Qualifier: X = No Qualification W = Wall F = Floor U = Upper M = Middle L = Lower C = Composite E = East Bank SW/SD C = Channel SW W = West Bank SW/SD * = Place Holder for Ground Water Qualifiers: D = Dissolved Metals (Filtered) T = Total Metals (Unfiltered)

Figure 5-2A: Site Identification and Field Sample Identification Codes
Main Post SSI and RI/FS
Fort Devens, Massachusetts

SITE IDENTIFICATION CODE (10 Characters)									
CHARACTER NUMBER									
1	2	3	4	5	6	7	8	9	10
Study Area Number:		Site Type: S = Surface soil B = Soil boring E = Test Pit/Excavation M = Monitoring well W = Surface water D = Sediment P = Wipe C = Concrete chip A = Asphalt V = Air G = Geoprobe	Hyphen	Year of activity		Hyphen	Location number: The number of the boring, surface soil, monitoring well, etc. sampling location		Shallow to deep designator for monitoring well clusters (A-D) X = All Samples and Wells

SAMPLE IDENTIFICATION CODE (8 CHARACTERS)							
CHARACTER NUMBER							
1	2	3	4	5	6	7	8
Sample Media and Technique (A-Z) A=Asphalt/Chip B=Soil/Drilling C=Concrete/Chip D=Sediment/Auger-Dredge E=Soil/Test Pit M=Ground Water/Well P=Surfaces/Wipe S=Soil/Hand Auger V=Air/Pump-Filter W=Surface Water/Bomb-Direct F = Soil/Geoprobe G = Ground Water/Geoprobe	Sample and QC Code (A-Z) X=Unfiltered Field Sample Y=Filtered Field Sample T=Trip Blank F=Field Blank R=Rinse Blank D=Unfiltered Field Sample Duplicate E=Filtered Field Sample Duplicate M=Matrix Spike Z=Matrix Spike Duplicate	Event Code (A-Z) A=Early Spring 1993 B=Winter 1993-1994 C=Spring 1994 D=Summer 1994 E=Fall 1994	Study Area (00-99) Use Fort Devens assigned SA Nos.		Sample Point (00-99) or (A-Z) Study Area or site location-specific sequential sample point location designators		Sample Depth or Orientation (0-9 or A-Z) U = Upper M = Middle L = Lower X = No Depth Z = Composite

6.0 Calibration Procedures and Frequency

6.1 Field Instrumentation

See Quality Assurance Project Plan.

6.2 Laboratory Calibration

See Quality Assurance Project Plan.

6.2.1 Laboratory Instrumentation Calibration

6.2.1.1 Calibration Standards. See Quality Assurance Project Plan.

6.2.1.2 Calibration Frequency. See Quality Assurance Project Plan.

6.2.1.3 Tuning and GC/MS Mass Calibration. See Quality Assurance Project Plan.

6.2.1.4 Decafluorotriphenylphosphine (DFTPP). See Quality Assurance Project Plan.

6.2.1.5 p-Bromofluorobenzene (BFB). See Quality Assurance Project Plan.

6.2.2 Operational Calibration

See Quality Assurance Project Plan.

6.2.2.1 General Calibration Procedures. See Quality Assurance Project Plan.

6.2.2.2 Method Blank. See Quality Assurance Project Plan.

6.2.2.3 Calibration Curve. See Quality Assurance Project Plan.

6.2.3 Calibration for USAEC Approved Methods

See Quality Assurance Project Plan.

7.0 Analytical Procedures

7.1 Analytical Program

See Quality Assurance Project Plan.

7.2 Laboratory Method Approval

See Quality Assurance Project Plan.

7.2.1 Laboratory Methods Requiring USAEC Approval

See Quality Assurance Project Plan.

7.2.2 Methods Not Requiring USAEC Approval

See Quality Assurance Project Plan.

7.3 Analyst Qualification

See Quality Assurance Project Plan.

7.4 Analytical Methods

See Quality Assurance Project Plan.

7.4.1 Sulfate and Chloride

See Quality Assurance Project Plan.

7.4.2 Volatile Organics (GC/MS)

See Quality Assurance Project Plan.

For air quality analysis, samples will be analyzed for volatile organic compounds (VOCs) in accordance with EPA Method TO-14, as described in *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air* (EPA Document 600/4-84-041).

A sample of ambient air will be drawn into a certified preevacuated SUMMA passivated canister. The sample will be analyzed using a high resolution gas chromatograph (GC). The VOCs are concentrated by collection in a cryogenically cooled trap. The cryogen is then removed and the temperature of the trap raised. The

VOCs are revolatilized, separated on a GC column, then detected by one or more detectors for identification and quantification.

7.4.3 Semivolatile (Acid/Base/Neutral) Organics (GC/MS)

See Quality Assurance Project Plan.

7.4.4 Organochlorine Pesticides/PCBs (GC/ECD)

See Quality Assurance Project Plan.

For air quality analysis, samples will be analyzed for PCBs in accordance with EPA Method TO-4, as described in *Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air* (EPA Document 600/4-89-017).

The samples will be extracted for 14 to 24 hours at 4 cycles/hour with 5 percent diethyl ether in hexane within one week after collection. The extracts will be concentrated to 10 mL and stored in a refrigerator until analysis. Analysis will be performed using GC/ECD as described in EPA Method 608. At least one PUF cartridge and filter that are not shipped to the field from each batch will be analyzed for the compounds of interest to serve as a process blank. One PUF cartridge and filter will be shipped to the field and returned to the laboratory, without drawing air through the sampler, to serve as a field blank. In addition, one solvent process blank will be analyzed.

7.4.5 Metals

7.4.5.1 Inductively Coupled Plasma Atomic Emission Spectroscopy (ICAP). See Quality Assurance Project Plan.

7.4.5.2 Cold Vapor (Mercury). See Quality Assurance Project Plan.

7.4.5.3 Graphite Furnace Atomic Absorption. See Quality Assurance Project Plan.

7.4.5.4 PM-10 and Metals (Air). For air analysis, samples will be analyzed for particulate matter and Target Analyte List metals. After measuring the particulate matter, Method 3051 will be used to digest the PM-10 filters. For analysis, Method 6010 (ICP) will be used for Al, Ba, Ca, Cd, Cr, Co, Cu, Fe, Pb, Mg, Mn, Ni, Ag, V, and Zn. Analyses by Graphite Furnace Atomic Absorption (GFAA) include Method 7041 for Sb, Method 7060 for As, Method 7091 for Be, and Method 7740 or 7471 for Cold Vapor Atomic Absorption (CVAA) will be used for mercury. Flame Atomic Absorption will be used for K (Method 7610) and Na (Method 7770).

7.4.6 Explosives

See Quality Assurance Project Plan.

7.4.7 TSS (Total Suspended Solids)
See Quality Assurance Project Plan.

7.4.8 TPHC (Total Petroleum Hydrocarbons) by Infrared
See Quality Assurance Project Plan.

7.4.9 TOC in Sediment by IR
See Quality Assurance Project Plan.

7.4.10 Total Phosphorous and Phosphate
See Quality Assurance Project Plan.

7.4.11 Total Kjeldahl Nitrogen (TKN) in Water by Automated Spectrophotometry
See Quality Assurance Project Plan.

7.4.12 Organophosphorus Pesticides
See Quality Assurance Project Plan.

7.4.13 Chlorinated Herbicides
See Quality Assurance Project Plan.

7.4.14 Nitrate
See Quality Assurance Project Plan.

7.4.15 Hardness
See Quality Assurance Project Plan.

7.4.16 Alkalinity
See Quality Assurance Project Plan.

7.4.17 Asbestos (Bulk) by Polarizing Light Microscopy
See Quality Assurance Project Plan.

7.4.18 Particle Size by Sieve Analysis
See Quality Assurance Project Plan.

7.4.19 TCLP Leachate Preparation
See Quality Assurance Project Plan.

7.5 Field Analytical Methods

See Quality Assurance Project Plan.

7.5.1 Total Petroleum Hydrocarbons by Non-Dispersive Infrared Spectrometry (NDIR)

See Quality Assurance Project Plan.

7.5.2 PCBs Using Immunosorbent Assay (Immunoassay)

See Quality Assurance Project Plan (Section 7.5.3).

8.0 Data Reduction, Validation, and Reporting

8.1 Arthur D. Little's Data Management

See Quality Assurance Project Plan.

8.1.1 Flow of Map Data into the IRDMIS

See Quality Assurance Project Plan.

8.1.2 Flow of Geotechnical Data into the IRDMIS

See Quality Assurance Project Plan.

8.1.3 Flow of Chemical Data into the IRDMIS

See Quality Assurance Project Plan.

8.2 Data Reduction

See Quality Assurance Project Plan.

8.3 Data Validation

See Quality Assurance Project Plan.

8.3.1 USAEC Data Validation Procedures

See Quality Assurance Project Plan.

8.3.2 USEPA Data Validation Procedures

See Quality Assurance Project Plan.

8.4 IRDMIS Record and Group Checks

See Quality Assurance Project Plan.

8.5 Data Reporting

See Quality Assurance Project Plan.

9.0 Internal QC Checks and Frequency

9.1 Control Samples

See Quality Assurance Project Plan.

9.2 Field Control Samples

See Quality Assurance Project Plan.

9.2.1 Trip Blanks
See Quality Assurance Project Plan.

9.2.2 Field Equipment/Rinsate Blanks
See Quality Assurance Project Plan.

The frequency of field equipment/rinsate blank collection is given in Table 4-2A.

9.2.3 Field Duplicates
See Quality Assurance Project Plan.

The frequency of field duplicate collection is given in Table 4-2A.

9.2.4 Field Blanks
See Quality Assurance Project Plan.

The frequency of field blank collection is given in Table 4-2A.

9.3 Laboratory Control Samples

See Quality Assurance Project Plan.

9.3.1 Laboratory Blanks
See Quality Assurance Project Plan.

9.3.2 Laboratory Duplicates
See Quality Assurance Project Plan.

9.3.3 Calibration Standards
See Quality Assurance Project Plan.

9.3.4 Spike Sample
See Quality Assurance Project Plan.

9.3.5 Internal Standard
See Quality Assurance Project Plan.

9.4 Concentration and Frequency of Control Samples

See Quality Assurance Project Plan.

9.4.1 Class 1 Certified Method
See Quality Assurance Project Plan.

9.4.2 Class 1A Certified Method (GC/MS only)
See Quality Assurance Project Plan.

9.5 Data Reporting for QC

9.5.1 Class 1, Class 1A, and Class 1B Certified Methods
See Quality Assurance Project Plan.

10.0 Performance and System Audits

10.1 Field Audits

See Quality Assurance Project Plan.

10.2 Laboratory Audits

See Quality Assurance Project Plan.

10.2.1 Data Review

See Quality Assurance Project Plan.

10.3 Project Audits

See Quality Assurance Project Plan.

11.0 Preventive Maintenance

11.1 Field Instruments

See Quality Assurance Project Plan.

11.2 Laboratory Equipment

See Quality Assurance Project Plan.

12.0 Procedures Used to Assess Data Accuracy, Precision, and Completeness

12.1 Lack of Fit (LOF) and Zero Intercept (ZI) Tests

See Quality Assurance Project Plan.

12.2 Certified Reporting Limit (CRL)

See Quality Assurance Project Plan.

12.3 Method Certification Accuracy

See Quality Assurance Project Plan.

12.4 Method Certification Standard Deviation

See Quality Assurance Project Plan.

12.5 Method Certification Percent Inaccuracy

See Quality Assurance Project Plan.

12.6 Method Certification Percent Imprecision

See Quality Assurance Project Plan.

12.7 Data Moving-Average Accuracy and Precision

See Quality Assurance Project Plan.

12.8 Control Charts

See Quality Assurance Project Plan.

12.8.1 Control Chart Plotting: Single-Day

See Quality Assurance Project Plan.

12.8.2 Three-Point Moving Average

See Quality Assurance Project Plan.

12.9 Out-of-Control Conditions

See Quality Assurance Project Plan.

12.10 Non-USAEC Methods

See Quality Assurance Project Plan.

12.11 Completeness

See Quality Assurance Project Plan.

13.0 Corrective Actions

13.1 Field Situations

See Quality Assurance Project Plan.

13.2 Laboratory Situations

See Quality Assurance Project Plan.

14.0 Quality Assurance Reports to Management

14.1 Laboratory Reports

See Quality Assurance Project Plan.

14.2 Program QA Officer and Lead Chemist Reports

See Quality Assurance Project Plan.