

3627

USATHAMA PAM 11-41
Revision No. 0

U S A T H A M A

U.S. Army Toxic and Hazardous Materials Agency

U.S. ARMY TOXIC AND HAZARDOUS
MATERIALS AGENCY

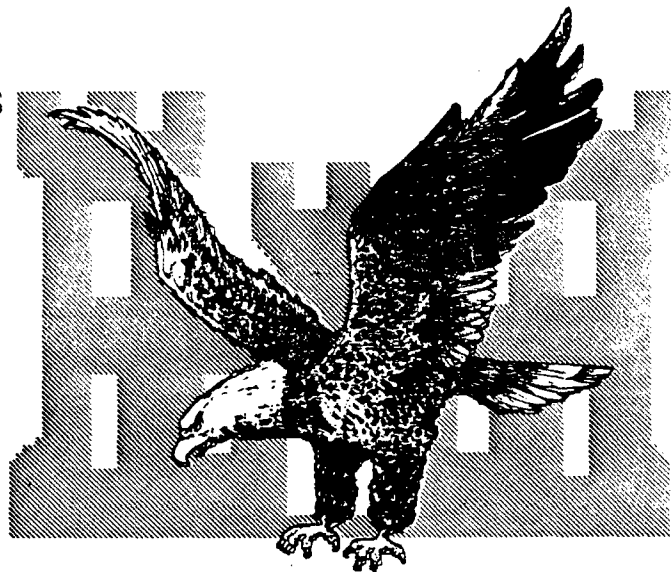
QUALITY ASSURANCE PROGRAM

JANUARY 1990

Prepared for

Commander

U.S. Army Toxic and Hazardous Materials Agency
Aberdeen Proving Ground, MD 21010-5401



20070419615

Distribution unlimited,
approved for public release

January 1990

USATHAMA PAM 11-41

Revision No. 0

U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
QUALITY ASSURANCE PROGRAM

JANUARY 1990

Prepared for

Commander

U.S. Army Toxic and Hazardous Materials Agency
Aberdeen Proving Ground, MD 21010-5401



THIS PAGE INTENTIONALLY LEFT BLANK



January 1990

USATHAMA PAM 11-41

Revision No. 0

DISCLAIMER

The mention/use of product or commercial names in this document does not constitute official endorsement of these products or producers by the Department of the Army.





January 1990

USATHAMA PAM 11-41

Revision No. 0

1.0 USATHAMA QUALITY ASSURANCE PROGRAM

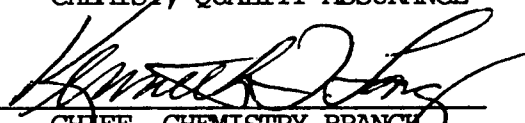
JANUARY 1990

APPROVED:



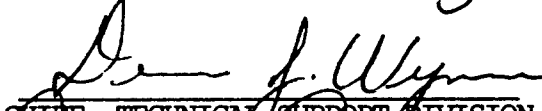
CHEMIST, QUALITY ASSURANCE

29 Jan 90
DATE



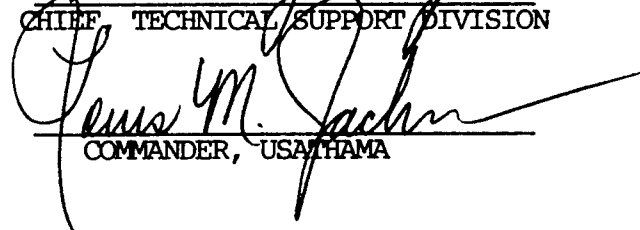
CHIEF, CHEMISTRY BRANCH

1/29/90
DATE



CHIEF, TECHNICAL SUPPORT DIVISION

1/29/90
DATE



COMMANDER, USATHAMA

2 Feb 90
DATE

U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY

ABERDEEN PROVING GROUND, MD 21010-5401



FOREWORD

This guidance document describes the Quality Assurance Program which shall be used by a performer in preparing a Project Quality Control (QC) Plan for the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) Installation Restoration projects. The Project QC Plan submitted in fulfillment of a project requirement should be a detailed, step-by-step document implementing the procedures described herein.

The concepts expressed in this document represent what is considered by USATHAMA to be the best approach for conducting and controlling chemical analyses. The prescribed principles and procedures are a result of considerations of general operations and trends in the field of analytical chemistry and of previous experiences in USATHAMA programs.

The Quality Assurance (QA) Program has been designed to be theoretically sound and operationally efficient. Although USATHAMA is sensitive to differences in laboratory practices, it is essential that all products submitted to USATHAMA for approval are in the formats prescribed in the QA Program.

Modifications to the guidance expressed in this document may be made only after specific approval, by USATHAMA, of the change. This flexibility will provide a means by which the QA Program may be updated as more experiences and knowledge become available in analytical chemistry and USATHAMA programs. This January 1990 Edition supersedes all previous Editions.



EXECUTIVE SUMMARY

The quality Assurance Program has been prepared following the organizational guidelines contained in the U.S. Army Environmental Protection Agency QAMs - 005/80. This program, therefore, has been completely reorganized when compared to the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) Quality Assurance (QA) Program, 2nd Edition, March 1987. The user is cautioned not to assume that everything in this current Edition of the USATHAMA QA Program is exactly the same as it was in the March 1987 Edition. Numerous updates and changes have been made. The major changes are documented in the following tables.





SUMMARY OF CHANGES

USATHAMA QA PROGRAM

SECTIONS

JANUARY 1990

<u>SECTION</u>	<u>CHANGES</u>
1.0	Signature page.
2.0	No change.
3.0	Emphasizes validation of data.
4.0	Requires project QC Plan to follow QAPjP format.
5.0	No change in precertification/certification requirements. Adds guidelines for personnel qualifications. Adds decertification criteria.
6.0	Adds guidelines for field personnel qualifications. Adds requirements for field SOPs.
7.0	Requirements for use of chain-of-custody procedures for all samples. Chain-of-custody procedures included within QA Program instead of as an Addenda. Adds requirement of samples receipt checklist.
8.0	No change in basic calibration requirements. Emphasizes requirements and criteria for check standards.
9.0	Adds requirements for laboratory SOPs. Adds requirement for program decision as to whether water samples are to be filtered or unfiltered.



10.0 Emphasizes transmission of laboratory records to USATHAMA at end of project.

Adds requirements for data deliverables.

Adds specifics on data packages and checklists.

Provides standard format for reporting GC/MS non-certified compounds.

Emphasizes requirements for data review and validation.

11.0 No change in requirement for control samples.

Adds validation of spiking solutions.

Adds modified control limits to control charting.

Adds requirement for tracking surrogate spike recovery.

12.0 Emphasizes USATHAMA audits and use of checklist.

13.0 No change in instrument maintenance requirements.

14.0 Requirements for statistics unchanged except for:

- Addition of criterion of detection and replacement of outliers during certification.

Increased emphasis on documentation.

15.0 No change in requirement for corrective actions.

16.0 No change in QA reports to management.



SUMMARY OF CHANGES
USATHAMA QA PROGRAM
APPENDICES
JANUARY 1990

APPENDICES CHANGES

A	Clarified requirements for documentation of analytical methods.
B	No change in LOF/Z1 statistics.
C	Updated statistical output for precertification/certification.
D	No change in documentation for method development.
E	No change in Rank Sum Test.
F	Added acceptance of sample containers commercially cleaned according to CLP procedures.
G	Defined SOPs for Field Operations.
H	Added Modifications to Holding Times for Volatiles and Explosives.
I	No change to SARM Repository Program.
J	Defined SOPs for Laboratory Operations.
K	No change in Outlier Testing.
L	Updated Control Chart Program Output.
M	Updated Control Chart Program Output.
N	Details Spiking Solution Control.
O	Defines and describes Modified Limits.



- P No major change in Performance Data Package Checklist.
- Q No major change in Control Chart Checklist.
- R No major change in Contractor QAC Checklist.
- S Adds requirement for Sample Receipt Checklist.
- T Adds Data Package Checklists.
- U Revised Audit Checklist.
- V Adds Calibration/Surrogate Documentation.
- W Added Items to Field Sampling Checklist.
- X Added Detection Limits for GC/MS Non-Certified Compounds.
- Y Describe procedure for rejection of outliers from certification data.

INDEX Revised.

USER EVALUATION SHEET Added.



2.0 TABLE OF CONTENTS

QUALITY ASSURANCE PROGRAM

1. Title Page
2. Table of Contents
3. Program Description
 - 3.1 Purpose
 - 3.2 Scope
 - 3.3 Application
4. Program Organization and Responsibilities
 - 4.1 Introduction
 - 4.2 Responsibility and Authority of USATHAMA
 - 4.3 Responsibility and Authority of the Contractor Laboratory Analytical Task Manager
 - 4.4 Responsibility and Authority of the Contractor QAC
 - 4.5 Project QC Plan
5. QA Objectives for Measurement Data in Terms of Precision, Accuracy, Completeness, Representativeness, and Comparability
 - 5.1 Introduction
 - 5.2 Analytical Methods
 - 5.3 Precertification Calibration
 - 5.4 Laboratory Certification
 - 5.5 Decertification
 - 5.6 Certification Samples



5.7 Certification Analyses

6. Sample Collection and Management

6.1 Introduction

6.2 Containers

6.3 Volatiles

6.4 Groundwater

6.5 Surface Water

6.6 Soils

6.7 Sediments

6.8 Sample Preservation

6.9 Standing Operating Procedures Field

6.10 Sampling

6.11 USATHAMA Sample Identification Numbers

7. Chain-of-Custody Procedures

7.1 Introduction

7.2 Survey Planning and Preparation

7.3 Sample Collection, Handling, and Identification

7.4 Transfer-of-Custody and Shipment

7.5 Laboratory Custody Procedures

7.6 Questions/Problems Concerning Custody Records

7.7 Evidentiary Considerations

8. Calibration Procedures and Frequency

8.1 Chemical Calibration Curves



- 8.2 Calibration and Check Standards
- 8.3 Reference Material
- 9. Sample Analysis
 - 9.1 SOPs Laboratory
 - 9.2 Sample Holding
 - 9.3 Sample Preparation/Filtration
 - 9.4 Sample Analysis
- 10. Data Reduction, Validation, and Reporting
 - 10.1 Record Keeping
 - 10.2 Laboratory
 - 10.3 Analytical Records
 - 10.4 Data Reporting
 - 10.5 Data Deliverables
 - 10.6 Data Management System
 - 10.7 Data Reporting For GC/MS Non-certified Compounds
 - 10.8 Data Review and Validation
- 11. Internal Quality Control Checks
 - 11.1 Introduction
 - 11.2 Control Samples
 - 11.3 Data Reporting for QC
 - 11.4 Control Charts
 - 11.5 Out-of-Control Situations
- 12. Performance and System Audits



- 12.1 External
- 12.2 Internal
- 13. Instrument Maintenance
 - 13.1 Calibration Identification
 - 13.2 Calibration Standards
 - 13.3 Calibration Frequency Schedule
 - 13.4 Examples
- 14. Specific Routine Procedures Used to Assess Data Precision, Accuracy, and Completeness
 - 14.1 Statistical Analysis of Precertification Performance Data
 - 14.2 Statistical Analysis of Certification Performance Data
 - 14.3 Documentation
- 15. Corrective Actions
- 16. Quality Assurance Reports to Management
- 17. Bibliography
- 18. Glossary
- 19. List of Acronyms

APPENDICES

- A. Format for Documentation of Analytical Methods
- B. Lack of Fit and Zero Intercept Tests
- C. Sample Output of USATHAMA Statistical Analysis Program Required for Precertification/Certification
- D. Documentation for Proposed Method Development
- E. Rank Sum Test



- F. Sample Container Cleaning Procedures
- G. Standing Operating Procedures Field Operations
- H. Sample Preservation Procedures and Holding Times for Aqueous and Solid Samples
- I. SARM Repository Program
- J. Standing Operating Procedures Laboratory Operations
- K. Outlier Test
- L. X-R Chart Data Tabulation and Graphing for Duplicate Spike Recovery
- M. X-R Chart Data Tabulation and Graphing for Three Point Moving Average Spike Recovery
- N. Spiking Solution Control
- O. Modified Limits
- P. Precertification/Certification Performance Data Package Checklists
- Q. Control Chart Checklist
- R. Contractor QAC Checklist
- S. Sample Receipt Checklist
- T. Data Package Checklists
- U. Audit Checklist
- V. Calibration/Surrogate Documentation
- W. Field Sampling Checklist
- X. Detection Limits for GC/MS Non-certified Compounds
- Y. Rejection of Outliers from Certification Data

Index

User Evaluation Sheet/Change of Address





3.0 PROGRAM DESCRIPTION

3.1 PURPOSE

The purposes of the QA Program are to:

- Provide a consistent framework for the generation of analytical data in support of the environmental programs conducted by the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA);
- Establish standard practices which permit interlaboratory comparison of data; and
- Establish procedures for demonstrating that analytical systems are in control.

More specifically, the objectives of the QA Program are to:

- Estimate the quality of each analytical system, including precision, accuracy, and sensitivity sufficient for the needs of each project;
- Assist in the early recognition of deficiencies which might affect the quality of data;
- Enable the Contractor Laboratory to identify and implement actions that are necessary to ensure the validity of laboratory data; and
- Require sufficient documentation to verify the quality of data submitted to USATHAMA.
- Validate data and define data usability.

3.2 SCOPE

This document outlines the purpose, policies, organization, and operations of the QA Program established to support chemical analyses conducted for USATHAMA projects. Implementation of this QA Program at all laboratories performing chemical analyses for USATHAMA will help to ensure the validity of data and provide a reliable foundation on which to base decisions.



In implementing the QA Program, it is important that the user understand the difference between QA and quality control (QC). QA refers to the system whereby an organization provides assurance that monitoring of quality-related activities has occurred. Frequently, QA is interpreted as a record keeping system to ensure documentation of all activities, including traceability, completeness, and security of documents.

QC refers to 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. QC activities must be conducted within a system of QA to ensure that proof of QC exists. Within USATHAMA projects, QA alone is insufficient. Implementation of the QA Program in the laboratory is designed to ensure that data are collected under in-control conditions, rather than simply to ensure documentation of poorly conducted analyses.

The USATHAMA QA Program is intended to establish a QA system and proper QC procedures.

3.3 APPLICATION

The emphasis of this QA Program is on activities which generate analytical chemical data. In this context, analytical chemistry includes those aspects of field sampling that may affect the chemical integrity of samples, as well as chemical laboratory activities.

Specific requirements are provided for the sampling and chemical analysis of groundwater, surface water, soil, and sediment samples. The general principles described herein are applicable to most field/laboratory exercises. Air sampling, biological sampling, radiological analyses, and geotechnical parameter analyses, while not specifically addressed in this document, are covered by the general principles described herein. The unique requirements of these analyses must be addressed in project specific QA Project Plans.

Documentation is an important part of any QA Program and therefore the USATHAMA QA Program is designed to meet all documentation requirements, including litigation requirements. Chain-of-custody procedures, documentation of geotechnical activities, QA of computer-related activities, and QA of engineering calculations will be followed and documented in project specific QA Plans.



4.0 PROGRAM ORGANIZATION AND RESPONSIBILITIES

4.1 INTRODUCTION

The Commander of USATHAMA is ultimately responsible for the quality of data collected in support of Agency projects. This responsibility is delegated to the Chemistry Branch and individual Project Officers/Project Chemists. The QA/QC guidelines described in this document have been developed to assure that data quality are documented and controlled by USATHAMA contractors and that responsibilities can be executed.

The Chemistry Branch is responsible for maintaining an active, ongoing system of QA. Project-specific QA/QC occurs at Contractor Laboratories which are conducting analyses for USATHAMA projects. Typically, contractor analyses are under the direction of a Contractor Analytical Task Manager who is responsible to a USATHAMA Project Officer through a Contractor Project Manager. A Contractor Quality Assurance Coordinator (QAC) is appointed by the Contractor Project Manager to be an independent reviewer of sampling and analysis activities.

The relationships between the organizations and personnel involved in QA/QC are shown in Figure 4-1.

4.2 RESPONSIBILITIES AND AUTHORITY OF USATHAMA

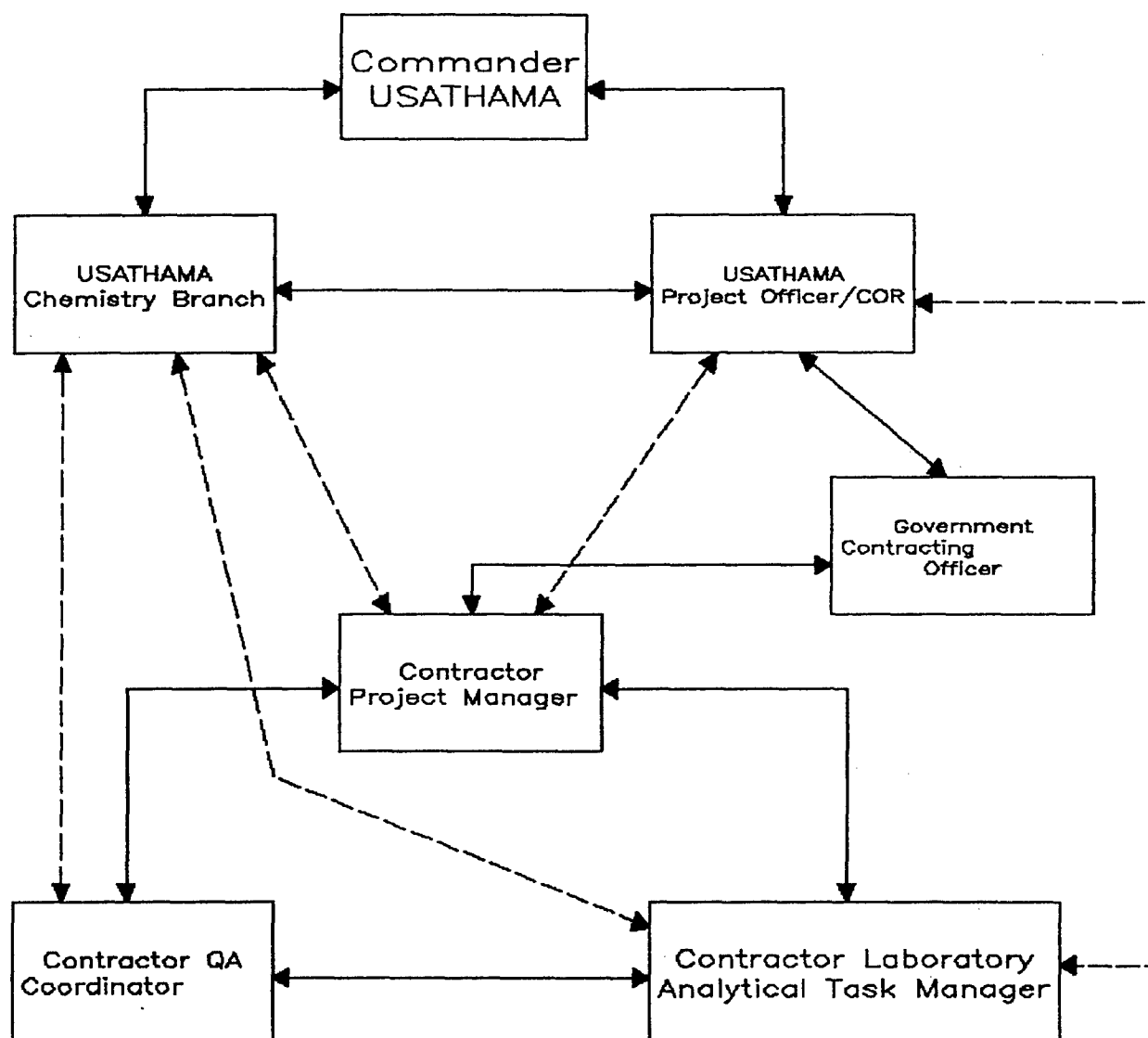
4.2.1 CHEMISTRY BRANCH, TECHNICAL SUPPORT DIVISION

The Chemistry Branch, Technical Support Division will:

- Advise the Commander on QA/QC practices;
- Recommend to the Commander QA practices to be used to support USATHAMA projects;
- Approve Project QC Plans (Section 4.5) submitted by Contractor Laboratories;
- Provide standardized analytical methods, if available, for specific analytes to Contractor Laboratories (Section 5.2);
- Provide analytical reference materials to Contractor Laboratories.



Figure 4-1. Lines of Communication for USATHAMA Projects



Formal Communication —————

Informal Communication - - - - -



- Supply Target Reporting Limits (TRL) to USATHAMA Project Officers based on the formal list of applicable analytes;
- Review and recommend approval of any proposed modifications to analytical methodology;
- Recommend certification of Contractor Laboratory analytical methods prior to collecting field samples;
- Provide guidance to USATHAMA Project Officers on implementation of QA/QC in Contractor Laboratories;
- Provide guidance to USATHAMA Project Officers on chemistry matters;
- Evaluate the quality of data generated by Contractor Laboratories;
- Monitor the effective implementation of QA/QC at Contractor Laboratories and report questionable practices to the Commander of USATHAMA;
- Conduct onsite audits of Contractor Laboratories;
- Conduct field audits of sampling activities;
- Review contractor technical plans for adequacy of analytical methods and QA/QC; and,
- Coordinate data reporting requirements with the USATHAMA Data Management Group.

4.2.2 PROJECT OFFICER

The Project Officer will where applicable:

- Act as the principal contact between USATHAMA and the Prime Contractor;
- Require effective implementation of the USATHAMA QA Program;
- Forward Chemistry Branch review comments to the Prime Contractor;
- Provide formal notification to the Contracting Officer of unapproved deviations from the QA Program;
- Ensure timely QC chart submission from the Prime Contractor on a weekly basis;



- Provide a formal list of applicable analytes for each project to the Chemistry Branch and Prime Contractor;
- Inform the Chemistry Branch of difficulties and problems encountered by the Prime Contractor in implementing the QA Program;
- Discuss proposed changes in approved sampling and analysis procedures with the Chemistry Branch;
- Provide project QC plans to the Chemistry Branch for review and approval;
- Provide certification documentation to the Chemistry Branch for review and approval; and,
- Notify Prime Contractor of certification status.

4.3 RESPONSIBILITIES AND AUTHORITY OF THE CONTRACTOR LABORATORY ANALYTICAL TASK MANAGER

The responsibility for implementing the USATHAMA QA Program resides with the Contractor Analytical Task Manager. This responsibility includes, but may not be limited to the following:

- Through the contractor Project Manager, submit to USATHAMA Project Officer or Contracting Officer's Representative for approval a detailed Project QC Plan specific to the USATHAMA project being supported;
- Support a 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 USATHAMA project and QA Program;
- Submit the required documentation and laboratory certification data to the USATHAMA Chemistry Branch prior to analyzing field samples;
- Ensure that subsampling and other handling procedures 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.

4.4 RESPONSIBILITIES AND AUTHORITY OF THE CONTRACTOR QAC

The QAC has the responsibility to establish, oversee, and audit specific procedures for documenting and controlling analytical data quality. Many of the procedures will be implemented by other individuals, but the QAC must ensure that procedures are being implemented properly and the results interpreted correctly. Appropriate QAC activities include, but may not be limited to the following:

- 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 Contractor Project Manager, Contractor Analytical Task Manager, and/or contractor laboratory management of nonconformance to the QA Program;
- Request analytical reference materials from USATHAMA through the USATHAMA Chemistry Branch;
- Ensure that all records, logs, standard procedures, project plans, and analytical results are maintained in a retrievable fashion;
- Ensure that copies of standard procedures, project plans, and standing operating procedures are distributed to all laboratory personnel involved in the project;
- Establish, with the analysts and the Contractor Analytical Task Manager, 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 sampling is conducted in a manner consistent with the QA Program and other USATHAMA guidelines. This responsibility includes making unannounced trips to the site to inspect the sampling where applicable. A minimum of coordination with the Contractor Analytical Task Manager prior to the unannounced inspection is acceptable. Each major type of sampling (e.g., groundwater, surface water, soil, sediment) will be inspected at least once per installation investigation. The visit must occur during the first sampling effort for each matrix. Additional inspections may occur at the discretion of the QAC, with approval of the



USATHAMA Project Officer and Contractor Project Manager. The QAC will document (Appendix U) each inspection and ensure that procedures described in the Scope of Work, Project Work Plan, and Project QC Plan are followed. The QAC has the authority to require resampling of any site whose sample integrity was determined to have been affected by faulty sampling procedures, after obtaining approval from the USATHAMA Project Officer or the Contracting Officer's Representative;

- 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 USATHAMA Installation Restoration Data Management System (IRDMS). 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 the USATHAMA Chemistry Branch on a weekly basis (Section 12.0);
- 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.



4.5 PROJECT QC PLAN

4.5.1 INTRODUCTION

Prior to initiating field sampling and analysis of environmental samples, the Contractor Laboratory shall develop a detailed Project QC Plan for the specific project being supported. The Project QC Plan will be submitted to the USATHAMA Project Officer or the Contracting Officer's Representative, who will forward the plans to the Chemistry Branch for approval. Although the QA Program outlines a system for verifying and maintaining a desired level of performance quality, the Project QC Plan must provide laboratory-specific descriptions of how the QA Program will be implemented.

4.5.2 PURPOSE

The purposes of the Project QC Plan are to:

- Establish function-specific responsibilities and authorities for data quality;
- Establish procedures to ensure that all data are collected under conditions of analytical system control;
- Establish procedures for recognizing and correcting out-of-control situations;
- Establish procedures to ensure that non-laboratory activities do not compromise analytical data quality; and
- Establish record keeping procedures commensurate with project data uses.

4.5.3 CONTENTS

The USATHAMA Chemistry Branch recognizes that implementation of this QA Program will vary between laboratories. The structure of the QA/QC organization will depend not only on laboratory differences, but also on the contractor's project structure. For these reasons, the Project QC Plan must address laboratory-specific and project-specific situations that are not addressed by the USATHAMA QA Program.



One situation, in particular, which is not addressed in this document is the use of a subcontractor laboratory for analysis. This situation is particularly critical if the prime contractor performs sampling, data management, and assessment activities. When such a project organization exists, the Project QC Plan must address the identity, relationships, authorities, responsibilities, and lines of communication between project personnel. Explicit coordination activities between, and decision-making authorities of, the project and laboratory QA/QC personnel must be described. Particular attention must be paid to sampling inspections, impact of field activities on sample integrity and data quality, decisions concerning need for resampling or reanalysis, and reporting of data to the prime contractor and USATHAMA. These elements are critical and may require substantial planning and interorganizational cooperation.

The Project QC Plan shall include, as a minimum, the following information and descriptions:

- Title page with provision for approval signatures;
- Table of contents;
- Project description;
- Project organization and responsibility;
- QA objectives for measurement data in terms of precision, accuracy, completeness, representativeness, and comparability;
- Sampling procedures;
- Sample custody;
- Calibration procedures and frequency;
- Analytical procedures;
- Data reduction, validation, and reporting;
- Internal quality control checks and frequency;
- Performance and system audits and frequency;
- Preventive maintenance procedures and schedules;
- Specific routine procedures to be used to assess data precision, accuracy and completeness of specific measurement parameters involved;



- Corrective action; and
- Quality assurance reports to management.

Included in the above should be the following information and descriptions:

- A statement of adherence or reference to the USATHAMA QA Program;
- A detailed account of how the contractor, in conjunction with any subcontractors, will implement the USATHAMA QA Program;
- A description of sampling team and analyst training in technical skills, standard QC, and essential elements of the USATHAMA QA Program;
- QC sample introductions and lot sizing;
- A description of applicable logs (field, instrument, sample, QC) and their use;
- Storage and use of analytical reference materials;
- A list of personnel responsible for data review and sequence of review prior to submittal; and
- A list of SOPs.

Not all of these items are addressed in this document, but are part of good laboratory practices and must be included in the Project QC Plan. Whenever possible and appropriate, names of individuals and step-by-step procedures should be provided. Any changes to an approved project QC Plan must be requested in writing and formally coordinated through the Project Officer or Contracting Officer's Representative. Written approval from the Chemistry Branch must be obtained prior to implementation of the requested change. In the event that timely implementation is essential, verbal approvals may be granted on a limited basis provided the changes do not impact on resources or costs. These informal requests for changes and approvals will be formalized immediately in writing in order to document the change.





5.0 QA OBJECTIVES FOR MEASUREMENT DATA IN TERMS OF PRECISION, ACCURACY COMPLETENESS, REPRESENTATIVENESS AND COMPARABILITY

5.1 INTRODUCTION

Before using an analytical method to analyze environmental samples, a Contractor Laboratory must demonstrate the ability to perform the method for specific analytes. Standardized analytical methods to be used will be provided by USATHAMA, if available, along with a list of the target analytes and often the concentration range of interest. The laboratory demonstrates its ability to perform the analysis for specified compounds using the standardized methods and, in the process, generates data to be used in establishing method reporting limits. These data also provide a baseline for establishing control limits for daily analyses and should, therefore, reflect typical analytical performance. If available, performance evaluation samples, (supplied from an independent source by direction of USATHAMA) covering the analytes and matrices required for the effort being tasked, will be analyzed and the results will be evaluated by the USATHAMA Chemistry Branch.

Laboratory certification is a two phase process involving an initial submission of data from precertification calibration standards, followed by a submission of data from certification performance samples. Certification is also contingent on acceptable laboratory audits, documentation of procedures and the laboratory managements commitment to the QA Program Plan. A typical sequence of certification activities is shown in Figure 5-1. The USATHAMA Chemistry Branch will determine whether the Precertification and Certification Performance Data Packages demonstrate proficiency of the laboratory in conducting a given analysis. Certification is for specific analytes over a given tested range determined by specific methods. Laboratories certified for one method or analyte are not automatically certified for any other analyses or analytes. Upon certification approval, USATHAMA will provide the laboratory with the correct method number to be used when reporting data.

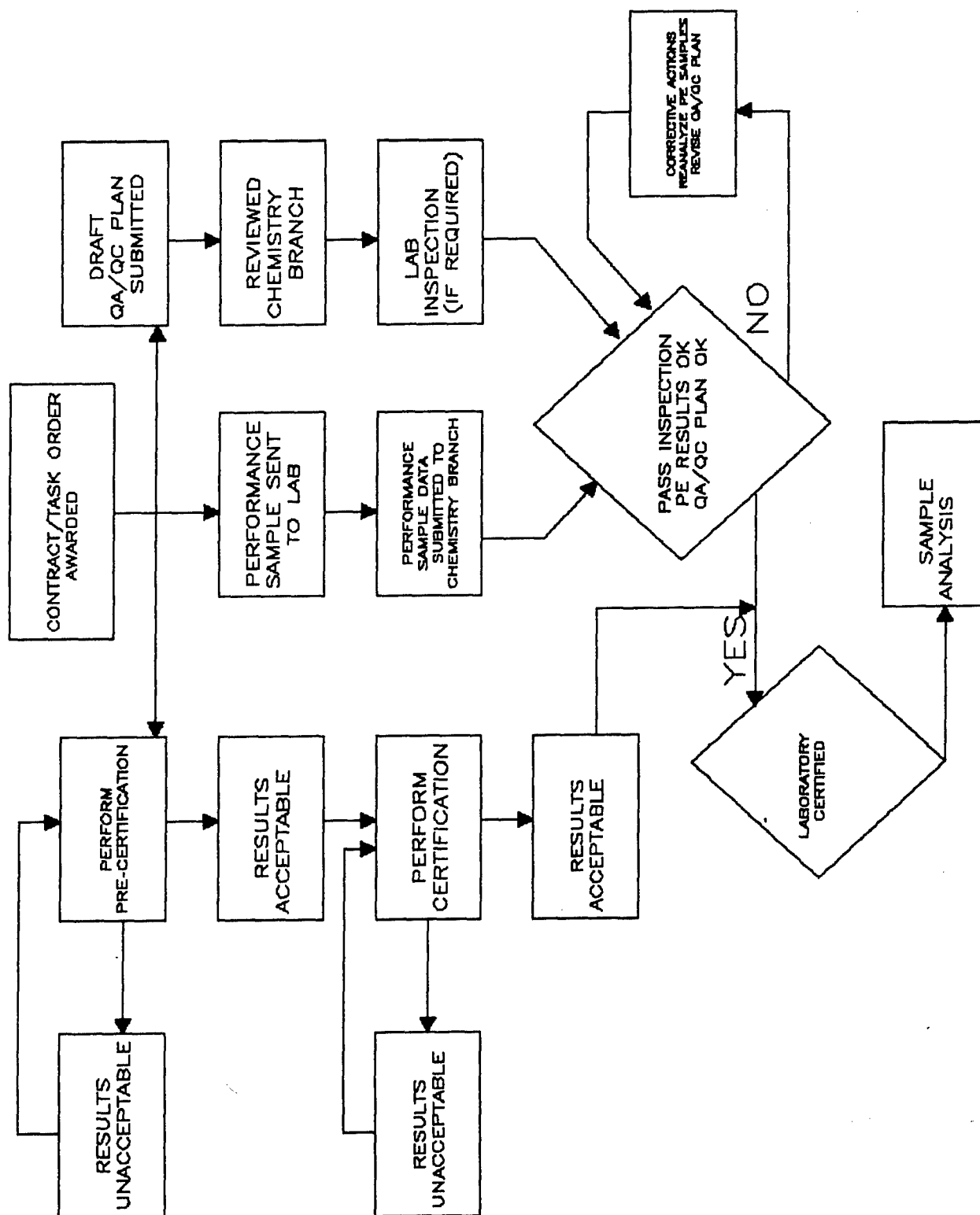
Due to constraints of sample holding times (Appendix H), collection of environmental samples shall never occur before all required analytical methods are certified.

5.2 ANALYTICAL METHODS

Any analytical method must be described by a set of written instructions completely defining the procedure to be used to process a sample and obtain an analytical result. Descriptions of analytes, sample type (matrix), sample



Figure 5-1.



preparation, types and quantities of reagents, instrumental calibration and measurements, and computations are all integral parts of a complete method. The standard format for documentation of all analytical methods is provided in Appendix A, and the format for data analysis is provided in Appendix C. The analytical method, as certified, shall be followed throughout the entire project. Changes to the certified method, regardless of how minor, must be approved in writing by the USATHAMA Chemistry Branch. The Chemistry Branch will determine how significant the change is and if recertification is required. The analytical methods selected for a particular task should closely approximate the EPA methods, if available, specified by the governing regulations (CERCLA, RCRA, etc.). Any method that offers the capability for analyte confirmation (e.g., second column confirmation for a GC method) shall have the confirmation procedure included as part of the method writeup. The confirmation procedure will require certification as a Class 2 method.

5.2.1 STANDARDIZED METHODS

In order to provide a common point of reference for all projects and to provide a means of evaluating laboratory performance, USATHAMA 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 (e.g., by EPA, ASTM, etc.; Refer to APHA-AWWA-WPCF, 1980; Federal Register, Part III, December 3, 1979; Federal Register, Part VIII, October 26, 1984; EPA, 1979b; EPA, 1982e; EPA, 1982f; EPA, 1982g; and U.S. Geological Survey, 1977b), USATHAMA standing methods or past USATHAMA 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. A description of any proposed deviations from the standardized methods must be submitted to USATHAMA prior to generation of the Precertification Performance Data Package. After certification of a method, additional deviations will not be acceptable, unless written approval, in advance, is provided by the USATHAMA Chemistry Branch. Any change in the documented procedure will constitute a modification. The significance of the modification will be determined by the USATHAMA Chemistry Branch. Changes made after certification may require generation of new Precertification and Certification Performance Data Packages. Methods specifically designated as Field Detection Methods should also follow the requirements of certification as described in this QA Program and contain the necessary statements/procedures for the associated QA/QC.



5.2.2 METHODS NOT REQUIRING CERTIFICATION

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, project QC plans, etc., to describe exactly the procedures to be used. A copy of the methods 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 (TOC);
- Biochemical Oxygen Demand (BOD);
- Chemical Oxygen Demand (COD);
- Total Dissolved Solids (TDS);
- Total Suspended Solids (TSS);
- Total Petroleum Hydrocarbons;
- Salinity;
- Total Solids;
- Acidity;



- Total organic Halogen (TOX); and
- Dissolved organic carbon (DOC).

Other methods that may be included in this category should be brought to the attention of the Chemistry Branch for consideration. Certification may be required for these types of analyses if the resulting data serves as the basis for project decisions or regulatory compliance. When a requirement exists to perform an analysis following strict adherence to the EPA Contract Laboratory Program (CLP), this will be accomplished under the category of non-certified analyses.

5.2.3 METHOD DEVELOPMENT

In the event that analyses must be conducted for compounds for which no reliable methods exist, development of a method will be conducted by a Development Laboratory (laboratory designated and/or contracted to develop an analytical method). Documentation for Proposed Methods Development (Appendix D) will be submitted to the USATHAMA Chemistry Branch for approval prior to initiation of development.

The Chemistry Branch will evaluate the proposed approach for technical soundness and economy of effort. The Chemistry Branch will then request the Development Laboratory to proceed with the method development, either as proposed or with USATHAMA recommended modifications.

The Development Laboratory will investigate the proposed procedures to be included in the method. Should any of the proposed procedures approved by the Chemistry Branch be found to be inadequate for the method, alternative procedures will be investigated after approval by the Chemistry Branch.

When testing of the analytical procedures has been successfully completed by the Development Laboratory, the method will be documented in the standardized format (Appendix A). In addition, the Development Laboratory will generate Performance Data Packages required for precertification and certification.

Full documentation of the method will be submitted to the USATHAMA Chemistry Branch. The Chemistry Branch will review the documentation for completeness and comprehension. Based on this review, the Development Laboratory will make any necessary modifications. After final approval by the Chemistry Branch, the method will be assigned a method number and issued as a standardized method.



5.3 PRECERTIFICATION CALIBRATION

Precertification calibration is performed in order to determine if the calibration model chosen is appropriate for the selected analytical method. Before initiating analyses, the Contractor Laboratory must discuss anticipated environmental concentrations with the Chemistry Branch, the USATHAMA Project Officer, and the Contractor Project Manager. For Class 1, Class 1A, and Class 1B methods, the concentration range tested during certification must include the TRL but may extend as high as desired, within the response range of the instrument adjusted at the sensitivity necessary to measure the TRL. For Class 2 methods, certification is performed at a single concentration level readily distinguishable from a blank. Because certification costs increase as the concentration range expands, the range to be used during certification must be discussed with the USATHAMA Project Officer, Contractor Project Manager, and USATHAMA Chemistry Branch. The concentration of the highest calibration standard shall exceed the certification range by an additional 10 percent (inorganic analyses) or 25 percent (all other analyses) and the concentration of the lowest calibration standard shall be 10 percent lower (inorganic analyses) or 25 percent lower (all other analyses) than the 0.5 TRL value of the certification range as allowance for fluctuations from a theoretical 100 percent method recovery. The calibration range established during precertification shall also be used during certification and subsequent sample analyses.

The Contractor Laboratory shall input data into USATHAMA supplied programs which tabulate and graph response versus concentration. The Contractor Laboratory will analyze precertification calibration curves for Lack of Fit (LOF) and Zero Intercept (ZI) (Appendix B). These data shall be submitted to the USATHAMA Chemistry Branch for evaluation. Approval of the Precertification Performance Data Package is required before certification may continue. While it is desired that the calibration curve be linear, deviation from linearity for certain analyses is not a problem as long as the calibration curve is correctly identified as to whether it is a quadratic or exponential, etc. Deviation from linearity will be a problem if the method being certified is known historically to result in linear calibration curves.

In addition to the Precertification Calibration standards (Class 1 and Class 1B methods only), certified calibration check standards, obtained from EPA or other commercial sources, shall be analyzed. The purpose of the calibration check standard is to determine any bias that may have been introduced in the preparation of the calibration standards and whether the calibration is performing as expected. During a Class 1 or Class 1B precertification, a calibration check standard shall be analyzed at the completion of the calibration run. The concentration of the calibration check standard shall be near the upper end of the calibration range and shall contain all analytes of interest. Calibration check standard results shall be within the limits of acceptability defined in Section 8.2. For multi-analyte methods at least 2/3 of the analytes must be within the limits of acceptability (see Table 11-2).

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 must be diagnosed and corrected, and precertification repeated.



5.4 LABORATORY CERTIFICATION

Laboratories, rather than individual analysts, must demonstrate proficiency in conducting chemical analyses by analyzing spiked standard samples using the analytical method intended for use in the USATHAMA project being supported. Although the proficiency of individual analysts is of concern to USATHAMA, it is the responsibility of the organization to establish personnel qualifications and training requirements for all positions. Each member of the organization shall have the education, training, technical knowledge, and experience, or a combination thereof, to enable that individual to perform assigned functions. Personnel qualifications shall be documented in terms of education, experience and training. Training shall be provided for each staff member as necessary to properly perform their functions. Poor data quality, as reflected in the Performance Data Package or daily out-of-control situations, may be caused by untrained or inexperienced analysts.

Guidelines to be used in the determination of personnel qualifications are as follows:

- Laboratory Director - should have earned a Baccalaureate Degree in Science or Engineering from an accredited college or university or the equivalent and have at least 5 years experience in laboratory work.
- Senior Staff - should have earned a Baccalaureate Degree in Science or Engineering from an accredited college or university or the equivalent and have at least 2 years experience at the bench level.
- Technical Staff - should have formal training in the sampling and analytical methodology and quality control as applied to the specific sample types and concentration levels of analytes which are of interest to the project.



Once a laboratory is certified to perform an analytical method for one USATHAMA project, the certification will normally suffice for other USATHAMA projects and need not be repeated unless certification requirements, methodologies, analytes, or required reporting limits have changed. Certification of a laboratory is not only dependent on the demonstration of method performance, as described in these sections, but is contingent on, but not limited to, review and approval of facilities and equipment, personnel, QC plan and standing operating procedures (SOPs). Continued certification will depend on the ability of the laboratory to meet control limits established during previous projects. Certification can be rescinded if a method is found to be unreliable, if a laboratory is found to have misrepresented certification data or methods, or if a laboratory proposes to conduct analyses by varying the procedure used during certification. Laboratories will be required to recertify before continuing to use a method if one of these situations occurs. In addition, recertification will be required for any analytical method held in abeyance for a period of two-years or greater. The recertification process, in this case, will be dependent on the statistical data base available for the method(s) in question. This will be discussed, on a case-by-case basis, with the USATHAMA Chemistry Branch.

5.5 DECERTIFICATION

A laboratory may be decertified for a specific method or all methods. Once decertified, a laboratory can no longer perform analysis using the decertified method, if it is only a method that was decertified; or can no longer perform analysis for USATHAMA if all methods were decertified and/or the laboratory was found to be out of compliance with the requirements of the USATHAMA QA Program. A laboratory may become recertified if, after review of documentation provided by the laboratory, the Chemistry Branch, Technical Support Division, and the USATHAMA Project Officer agree to allow the recertification. The provided documentation must include, but not be limited to, a plan for the elimination or correction of the cause(s) for decertification.

Decertification of a method may occur for, but not only limited to, the following reasons: if the method is found to be unreliable; if certification data were found to have been misrepresented; if the procedure has been modified without prior approval from USATHAMA Chemistry Branch; if established control limits cannot be met or there is a process shift in the data where the method parameters are no longer valid; or if improprieties were discovered in the representation of method performance.

Decertification of a laboratory for all methods may occur for, but are not limited to, the following:



- Decertification of multiple methods for the reasons enumerated above;
- Lack of compliance with the USATHAMA QA Program;
- Repeated failure of laboratory audits;
- Changes in facilities, equipment or personnel that impact on the performance of the analyses;
- Failure of management to meet requirements including, but not limited to, meeting sample holding times, timely submission of control charts and/or data, submission of reports;
- Improperities in the development of data;
- Failure to maintain documentation in accordance with requirements; and
- Failure to follow and comply with approved SOPs.

5.6 CERTIFICATION SAMPLES

Unlike some agencies, USATHAMA does not provide test samples (i.e., performance evaluation) to a laboratory. However, if samples become available through another agency (i.e., EPA) they will be required to be analyzed. The analysis of performance evaluation samples does not replace the analysis of certification samples, as described in this program, but are an addition to the USATHAMA program. Samples necessary for certification performance are prepared in the Contractor Laboratory to assure that the same neat reference material is used in preparing the stock solutions for spiking the standard samples during certification and as a primary standard for the QC samples during environmental sample analysis.

5.6.1 STANDARD WATER SAMPLES

Standard water samples will be prepared by adding a known quantity of target analyte to a known volume of water. The volume of water will be specified in the method being performed. All target analytes for the method will be added. ASTM Type I grade water will be used for inorganic methods. ASTM Type II grade water containing 100 mg/L each of added sulfate and chloride will be used for organic methods (Table 5-1). The method and reagents used to prepare spiking solutions are specified in the standardized methods.



5.6.2 STANDARD SOLID SAMPLES

Standard solid samples will be prepared by adding a known quantity of target analyte to a known weight of selectively blended standard soil as provided by the Chemistry Branch. This standard soil is provided to the Contractor Laboratory after contract award. The required amount of soil (sample weight) to be spiked will be specified in the method being tested. A minimum quantity of solvent shall be used so that the character of the sample is not changed. All target analytes for the method will be added. With the exception of volatiles, spikes must sit in contact with soil for a minimum of 1 hour before processing of the sample continues. The method and reagents used to prepare spiking solutions are specified in the standardized methods. The Contractor Laboratory will be provided a sufficient quantity of this standard soil to last for the duration of the project or series of projects.

5.7 CERTIFICATION ANALYSES

Methods may be certified in four different ways (Class 1, Class 1A, Class 1B, or Class 2), depending on specific project requirements and analytical method types, subject to prior USATHAMA approval. The difference between classes is the procedure used to characterize laboratory performance of the method. Class 1A certification is reserved exclusively for GC/MS methods while Class 1B is reserved for low sample throughput methods (non GC/MS). Designation of a method as Class 1B can only be made by the USATHAMA Chemistry Branch following the review and approval of a written request to do so from the laboratory. Data generated during certification testing are subject to outlier testing in order to remove anomalies from the data set that can incorrectly affect the resulting certified reporting limit calculation. As the calculations are based on having an equal number of responses for each target concentration, statistically valid replacement values must be supplied, where required. For Class 1 and 1B certifications, no more than one datum at a given concentration and no more than two values total should be rejected from a set. If the two values occurred on the same day, a repeat of that days certification shall be performed. For Class 1A certification, no more than one outlier can be rejected from a set. The procedure for the rejection of outliers from certification data is detailed in Appendix Y. Both the data set including the outlier and the corrected data set shall be supplied with the certification package.

5.7.1 CONCENTRATION RANGE

For each analyte/method combination, a TRL must be chosen before starting analyses. The TRL will be specified whenever possible, by the USATHAMA



Table 5-1. CRITERIA FOR ASTM WATER TYPES

Grade of Water	Maximum Total Matter (mg/L)	Maximum Electrical Conductivity at 25C (umho/cm)	Minimum Electrical Resistivity at 25C (M cm)	Minimum Color Retention Time of KMnO ₄ (min)
Type I	0.1	0.06	16.67	60
*Type II	0.1	1.0	1.0	60

* 100 mg/L Sulfate and Chloride Added. The following preparation is provided:

- (1) Weigh 1.48 g of reagent grade anhydrous sodium sulfate into a 1-liter volumetric flask and dilute to mark with ASTM Type II water.
- (2) Weigh 1.65 g of reagent grade anhydrous sodium chloride into a 1-liter volumetric flask and dilute to mark with ASTM Type II water.
- (3) Transfer 100 ml of each solution prepared in (1) and (2) into a 1-liter flask and dilute to volume with ASTM Type II water.



Chemistry Branch, based on the technologically obtainable lowest method detection limits and regulatory environmental quality criteria to meet the data quality objectives of the task. A list of typical TRLs that may be specified for certification of target analytes is maintained by the Chemistry Branch. This list may be updated as a result of specific requirements or technology improvements.

The calibration range of the instrument must bracket the actual tested concentration range of the samples (certification and field) and is the range within which all instrumental measurements must be made during subsequent analyses. In no instance may the tested range be established or expanded by diluting certification samples, since all samples are required to be processed through a single procedure. If necessary, certification of two separate methods may be required for a range extension. Environmental sample extracts containing concentrations above the tested range shall be diluted to be within the certified range (certified reporting limit (CRL) to maximum tested concentration) for measurement.

The minimum testing range for Class 1 and Class 1B certification will always be the following:

- Blank;
- 0.5 times the TRL;
- 1.0 times the TRL;
- 2.0 times the TRL;
- 5.0 times the TRL; and
- 10.0 times the TRL.

The minimum testing range for Class 1A certification will always be the following:

- Blank;
- 0.5 times the TRL;
- 2.0 times the TRL; and
- 10.0 times the TRL.

Each order of magnitude increase above the minimum testing range must include three additional concentrations (e.g., 20, 50, 100; 200, 500, 1,000) for Class 1 and Class 1B, and two additional concentrations (e.g., 50, 200;



500, 2000) for Class 1A, at multiples of the TRL. Range extensions of less than one order of magnitude are acceptable. Extension of the range beyond the minimum testing range must be approved by the USATHAMA Project Officer and the USATHAMA Chemistry Branch.

Numbers and concentrations of samples to be analyzed during certification for different ranges and different certification classes are summarized in Table 5-2.

5.7.2 CLASS 1, CLASS 1A, AND CLASS 1B CERTIFICATION

Class 1, Class 1A, and Class 1B certified methods are used in USATHAMA projects to quantify analytes in various matrices. The results for environmental samples analyzed by Class 1 and Class 1B certified methods may generally be reported to three significant figures. In no instance may more than three significant figures be used. For Class 1A certified methods, environmental sample results for noncertified analytes shall be reported to one significant figure; however, certified analyte results may be reported to two significant figures.

All certification analyses must be preceded by instrument calibration, as described in Section 8.1. Before starting certification analyses, Initial Calibration (Section 8.1.1) must be performed. Calibration on subsequent days shall correspond to Daily Calibration (Section 8.1.2). If the Daily Calibration fails to meet acceptability criteria, Initial Calibration must be performed before continuing.

CLASS 1 AND CLASS 1B CERTIFICATION:

During certification, a minimum of one standard sample at each concentration shall be analyzed each day for 4 separate days. Sample spikes at each concentration for each day shall be prepared from a master stock solution that was prepared separately and independently from the calibration master stock solution. These master stock solutions (certification and calibration) shall be prepared on separate occasions by different personnel using identical procedures. The preparation of separate stock solutions not only will assist in the determination of bias in the preparation of standards but will help in the determination of solution degradation.

The 4 days of analysis shall be consecutive or as close to consecutive as possible. The placing of certification samples and calibration standards on an autosampler and allowing analysis to proceed over four periods of time



Table 5-2. NUMBERS AND CONCENTRATION OF CERTIFICATION SAMPLES

CLASS 1/CLASS 1B

Minimum Testing Range (MTR): 24 Certification Samples

Blank, 0.5, 1, 2, 5, & 10 TRL (4 Days)

MTR + 1 Order of Magnitude Extension: 36 Certification Samples

Blank, 0.5, 1, 2, 5, 10, 20, 50, & 100 TRL (4 Days)

MTR + 2 Orders of Magnitude Extension: 48 Certification Samples

Blank, 0.5, 1, 2, 5, 10, 20, 50, 100, 200, 500, & 1000 TRL (4 Days)

CLASS 1A

Minimum Testing Range (MTR): 8 Certification Samples

Blank, 0.5, 2, & 10 TRL (Duplicate)

MTR + 1 Order of Magnitude Extension: 12 Certification Samples

Blank, 0.5, 2, 10, 50, & 200 TRL (Duplicate)

MTR + 2 Orders of Magnitude Extension: 16 Certification Samples

Blank, 0.5, 2, 10, 50, 200, 500, & 2000 TRL (Duplicate)

CLASS 2

Minimum Testing Range: 8 Certification Samples

Blank, 1 TRL (Quadruplicate)



is NOT an acceptable alternative to analysis each day for 4 days. Analysis refers to performance of the entire method, including spiking samples and sample preparation, not merely to instrumental measurement.

The CRL and the method accuracy for each analyte shall be calculated by the Contractor Laboratory using a software program based on the equations outlined in Section 14 and supplied by USATHAMA. Data generated over the 4 days of analysis shall be used in the calculations.

Class 1A Certification:

During certification, a minimum of two standard samples at each concentration shall be analyzed on a single day. Sample spikes at each concentration shall be prepared from a master stock solution that was prepared separately and independently from the calibration master stock solution (see Class 1 and Class 1B certification).

Analysis refers to performance of the entire method, including spiking samples and sample preparation, not merely to instrumental measurement.

The CRL and the method accuracy for each analyte shall be calculated by the Contractor Laboratory using a software program based on the equations outlined in Section 14 and supplied by USATHAMA. Data generated over the single day of analysis shall be used in the calculations.

5.7.3 CLASS 2 CERTIFICATION

Class 2 certification is used for methods which screen for the presence or absence of contaminants. The results for samples analyzed by Class 2 certified methods are measured in relation to the TRL set to a desired action level and reported as "less than, equal to, or greater than" the TRL. A tested concentration range is not applicable since only the TRL concentration is tested. Upon successful completion of certification, the TRL becomes the CRL.

All certification analyses must be preceded by instrument calibration, as described in Section 8.1.4. During certification a minimum of four standard sample blanks and four standard samples spiked at the TRL shall be analyzed in a single day using the complete analytical method. The results of these analyses shall be subjected to the rank sum test (Appendix E) to determine if the spike level can be differentiated from the blank. After analyzing the eight standard samples and obtaining a positive or negative response for each, the results are arranged according to response. All negatives are listed, followed by positives. Ranks (ordinal numbers starting with one) are assigned to the responses. The mean of the ranks for each group of positive and negative results will be assigned to each response in the group. The sum of the ranks from the blanks shall not exceed 10 for acceptable certification.



If the analytical results from the 8 samples (4 spikes and 4 blanks) fail the certification test, 4 additional samples (2 spikes and 2 blanks) shall be analyzed. The analytical results from the additional blanks and spikes will be combined with the results from the original 8 samples. The resultant 12 responses will be subjected to the rank sum test as outlined previously. For acceptable certification using 12 responses, the sum of the ranks from the blank samples shall not exceed 26 (Appendix E).

If the testing again fails certification, the method is considered incapable of distinguishing between blanks and the spiked concentration level. The TRL concentration must then be increased to a level at which the method is capable of distinguishing the spikes from the blanks. If the TRL cannot be altered, another analytical method must be selected to obtain the desired sensitivity.



6.0 SAMPLE COLLECTION AND MANAGEMENT

6.1 INTRODUCTION

The procedures described in this section are designed to obtain samples which are proper representations of the sampled matrix. Trace levels of contaminants from sources external to the sample must be eliminated through the use of good sampling techniques. Sample management and stringent documentation are the key factors in a successful QA program for sampling.

This section does not discuss sampling of air, biological, or surface matrices or sampling for radiological constituents. When these matrices or analytes are included in a project, detailed requirements and protocols will be provided on a case-by-case basis. References are provided in the Bibliography which should be consulted when planning air or biological sampling (ASTM, 1973; EPA, 1974; EPA, 1976; EPA, 1977b; EPA, 1977c; EPA, 1978; EPA, 1983c; EPA, 1983d; U.S. Geological Survey, 1977a; and Weber, 1973).

Sampling requirements vary according to the analytes of interest and the environmental matrices sampled. These differences are discussed in Section 6.4 to 6.8. Section 6.3 discusses sample containers and Section 6.8 discusses sample preservation. References are provided in the Bibliography that discuss appropriate sampling methods in detail. These references should be consulted when preparing sampling plans (Barcelona et al., 1984; Nielson and Yeates, 1985; EPA, 1977a; EPA, 1980c; EPA, 1982a; EPA, 1982b; EPA, 1982d; EPA, 1983b; EPA, 1984a; EPA, 1984c; and U.S. Geological Survey, 1977b).

Documentation of sampling activities is described in Section 10.0.

6.2 PERSONNEL

It is the responsibility of the organization to establish personnel qualifications and training requirements for all positions. Each member of the organization shall have the education, training, technical knowledge, and experience, or a combination thereof, to enable that individual to perform assigned functions. Personnel qualifications shall be documented in terms of education, experience, and training. Training shall be provided for each staff member as necessary to properly perform their functions. The suggested minimum qualifications are as follows:

- Geologist - Baccalaureate Degree in Geology, Geotechnical Engineering, or Geohydrology.
- Sampler 3 - High School Degree or equivalent plus 40 hours of OSHA training plus at least 16-hours instruction in sample collection



techniques.

- Sampler 2 - All requirements for Sampler 3 plus 6-months experience (minimum participation in 3 sampling events) as Sampler 3.
- Sampler 1 Team Leader - All requirements of Sampler 2 plus 4-hour class in chain-of-custody procedures plus 6-months experience (minimum participation in six sampling events) as Sampler 2. A Baccalaureate Degree in an Engineering or Science related subject is desirable.

6.3 CONTAINERS

For water samples, the sample container shall be chosen to be compatible with the analyte(s) of interest. A complete list is provided in Appendix H. In general, however, the following containers should be used (exceptions will be noted in the standardized method):

- 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.

Wide-mouth amber-glass bottles shall be used for all soil and sediment samples.

All sample containers shall be cleaned before use according to the protocols specified in Appendix F. This procedure is intended for new containers as received from a vendor. Reuse of sample containers is not permitted. Purchasing commercially pre-cleaned bottles may be acceptable provided that cleaning is performed as specified in Appendix F or meets the requirements of the EPAs' Contract Laboratory Program. Documentation for commercial bottle cleaning procedures shall be submitted to USATHAMA for approval prior to implementation.



6.4 VOLATILES

6.4.1 GROUND/SURFACE WATER SAMPLES

When sampling water for volatile compounds, extra care must be exercised to prevent analyte loss by evaporation. Precautionary measures include:

- Acquiring the sample with equipment that minimizes water gas/liquid interphase under pressure or vacuum;
- Avoiding aeration or agitation of the sample to the greatest possible extent;
- Triple rinse sample vial with sample water;
- Taking duplicate samples, as a minimum;
- Filling vials to capacity, taking care that no air bubbles are trapped in the vial;
- Preserving to pH 2 with sodium bisulfate or HCl;
- Storing the sample at 4°C;
- Analyzing the sample as soon as possible, but never exceeding the prescribed holding time (Appendix H);
- Never allowing a volatile sample to freeze; and
- Never filtering the sample.

6.4.2 TAP WATER SAMPLES

The following procedures are to be used in the sampling of water from taps located anywhere in a water supply system:

- Water should be allowed to run from the tap for 2 to 3 minutes before sampling;
- Triple rinse sample vial with sample water;
- Slow the water flow to a trickle before filling the sample vial;



- Fill vial to the top, forming a water bulge above the rim. Add sodium thiosulfate to stop the chlorine reaction, as required. Screw on the cap without dislodging the teflon liner;
- Turn vial over and tap gently against a hard surface or hand. If air bubbles are trapped in the vial, discard and take another sample. Repeat until duplicate samples, free of air bubbles, are obtained; and
- As each vial is correctly filled, enter the applicable information on the label and then pack the vial into the shipping container. The contents of the shipping container must be kept at the required temperature at all times.

6.4.3 SOIL AND SEDIMENT SAMPLES

The sampling method for volatiles in soil or sediment will depend on the chemical analysis procedure and the nature of the soil or sediment. Portions of soil may be placed in empty vials containing the extraction solvent. In other instances, sealed cores may be shipped to the laboratory for subsampling.

The primary considerations for acquiring samples for volatiles, either in the field or in the laboratory, include the following:

- Samples stored at 4°C;
- Sample handling should be minimized;
- Sample/air contact should be minimized;
- Air-tight seals on all containers used in shipment or laboratory workup; and
- The sample or subsample should be placed in an air-tight container immediately after collection.



6.5 GROUNDWATER

All groundwater sampling will occur after the wells have been developed according to the USATHAMA Geotechnical requirements document and/or specifications in the contract. Because drilling and well construction disturb the natural groundwater system, the maximum possible length of time (never less than two weeks) shall pass between well development and sampling to allow the groundwater system to return to chemical equilibrium.

All equipment used to measure and sample the groundwater system (e.g., bailers, pumps, tapes, ropes) must be cleaned before use in each well to prevent cross contamination between wells. Equipment that is dedicated to a well site may not require cleaning between sampling events. If the well is free of inflowing sediments, thorough rinsing will be sufficient. When inflowing sediments adhere to equipment, scrubbing may be required in addition to rinsing. In no instance shall detergents, soaps, or solvents be used to clean equipment in the field.

Water used for rinsing field equipment shall be bottled distilled water or water from a USATHAMA-approved source. Such USATHAMA-approved water should originate from an uncontaminated (background) and untreated source. The water shall be analyzed by a USATHAMA-approved laboratory for all project specific analytes prior to collection of field samples. Water from chemical supply companies or retail merchants is acceptable, provided that analysis reveals such water is free of interferences. At least one sample must be submitted to the laboratory and be analyzed for all analytes of interest prior to the first use in the field. The initial rinse water analyses may be done prior to certification approval provided that the analytical procedures used are identical to those tested during certification. A rinse blank shall be included with the initial lot of samples during the initial and subsequent sampling excursions, defined as the time between mobilization and demobilization of the sampling team. Additional rinse blanks shall be taken, as required, to meet the DQOs' of the project. Waivers to these requirements will be considered by the USATHAMA Chemistry Branch on a case-by-case basis.

Sampling equipment must be protected from ground surface contamination. Clean plastic sheeting spread around the well is one means of protecting the equipment. New protective sheeting should be used at each sampling location. Sampling efforts shall preclude wind-blown particles from contaminating the sample or sampling equipment.

6.5.1 MONITOR WELLS

The following procedures incorporate the necessary aspects of sampling QA and shall be used each time a monitor well is sampled:

- Measure the depth from the top of the well casing (not protective casing) to the top of the water and record the depth in the sampling



logbook;

- Measure and record the depth from the top of the casing to the bottom of the sediment/water interface;
- Subtract the depth to top of the water from the depth to the bottom of the sediment/water interface to determine the height of standing water in the casing and saturated annulus. Remember to have on hand the diameter, height, and porosity of the sand pack, as recorded by the geologists during well construction;
- Obtain a sample of groundwater for temperature, conductivity, and pH measurements. Record these measurements in the sampling logbook;
- Remove a quantity of water from the well equal to 5 times the calculated volume of water in the well, including the saturated annulus;
- If the well goes dry during pumping or bailing, one is assured of removing all water which had prolonged contact with the well casing or air. If the recovery rate is rapid, allow the well to recover to its original level and evacuate a second time before sampling. If recovery is very slow, samples may be obtained as soon as sufficient water is available;
- Obtain samples for chemical analysis immediately after pumping or bailing is complete. For slow recovering wells, the sample shall be collected immediately after a sufficient volume is available;
- After obtaining chemical analysis samples, draw a second sample for temperature, conductivity, and pH measurement and record results in the sampling logbook;
- Filter samples, as appropriate; sample to be analyzed for VOCs should never be filtered;
- All samples must be placed in containers that have been cleaned according to the protocols in Appendix F. Samples for organic analyses shall be placed in clean amber-glass bottles with Teflon-lined lids. Samples for inorganic chemical analyses shall generally be placed in clean polyethylene bottles. Samples for volatile organics shall be placed in septum-sealed vials. The sample bottle and cap shall be triple rinsed with the water being sampled before filling the bottle with the sample to be analyzed. Bottles for filtered samples shall be rinsed with filtered sample water and bottles for unfiltered samples should be rinsed with unfiltered sample water;



- Add the appropriate preservative and cap securely;
- Label samples in accordance with Section 6.11; and
- Place sample bottle(s) in a temperature controlled (4°C) chest immediately after sampling and deliver to the laboratory as soon as possible.

Note that the rinsing requirement specifically precludes adding preservative to bottles before they are shipped to the sampling site. The sampling team must have available the correct preservatives and must be trained in handling and dispensing the preservatives (Field Sampling Checklist, Appendix W).

6.5.2 WATER SUPPLY WELLS

The following procedures incorporate the necessary aspects of sampling QA and shall be used each time a water supply well is sampled:

- From existing well data or an estimated well depth, calculate the maximum possible volume of water in the well casing;
- Obtain a sample of groundwater for temperature, conductivity, and pH measurements. Record these measurements in the sampling logbook; and
- Pump to discard at least 5 times the estimated volume of water in the well.

Prior to taking samples, ensure that the water to be sampled is raw (untreated) water. Under no circumstances should treated water be taken for chemical analysis to define the levels of contamination in the aquifer. If holding or pressure tanks are used in the water supply system, they should be bypassed to obtain good representative groundwater samples:

- Filter samples, as appropriate; samples to be analyzed for VOCs should never be filtered;
- All samples must be placed in containers that have been cleaned according to the protocols in Appendix F. Samples for organic chemical analyses shall be placed in clean amber glass bottles with Teflon-lined lids. Samples for inorganic chemical analyses shall generally be placed in clean polyethylene bottles. Samples for volatile organics shall be placed in septum-sealed vials. The sample bottle and cap shall be triple rinsed with the water being sampled before filling the bottle with the sample to be analyzed. Bottles for



filtered samples should be rinsed with filtered sample water and bottles for unfiltered samples should be rinsed with unfiltered sample water;

- Add the appropriate preservative and cap securely;
- Label samples in accordance with Section 6.11;
- Place sample bottle(s) in a temperature controlled (4°C) chest immediately after sampling and deliver to the laboratory as soon as possible; and
- After obtaining chemical analysis samples, draw a second sample for temperature, conductivity, and pH measurements and record results in the sampling logbook.

Note that the rinsing requirement specifically precludes adding preservative to bottles before they are shipped to the sampling site. The sampling team must have available the correct preservatives and must be trained in handling and dispensing the preservatives.

6.5.3 TAP WATER

The following procedures are to be used in the sampling of water from taps located anywhere in a water supply system:

- Water should be allowed to run from the tap for 2 to 3 minutes before sampling;
- Triple rinse sample vial with sample water;
- Each sample container must be completely filled with the water sample;
- Conductivity, pH, and temperature measurements, if required, must be performed on the water samples collected for inorganics analysis; and
- As each vial is filled, enter the applicable information on the label and then pack the vial into the shipping container. The contents of the shipping container must be kept at the required temperature at all times.

Note that the rinsing requirement specifically precludes adding preservative to bottles before they are shipped to the sampling site. The sampling team must have available the correct preservatives and must be trained in handling and dispensing the preservatives. If drinking



water quality is to be determined, the sampled tap(s) must be located after any water treatment processes.

6.6 SURFACE WATER

Surface water samples may be obtained under many different circumstances. At the time of sampling, the procedures described in the Project QC Plan and Project Workplans shall be followed. These documents must have designated the appropriate techniques for the project-specific setting, as described in Section 6.1.

Before sampling, equipment shall be rinsed downflow or away from the sampling point, taking care not to disturb sediments at the sampling point. After sampling each location, the equipment shall be rinsed with distilled water or USATHAMA-approved water, as discussed in Section 6.5.

All samples must be placed in containers that have been cleaned according to the protocols in Appendix F. The need for sample filtration will be determined according to the requirements given in Section 9.3.1. Samples for organic chemical analyses shall be placed in clean amber-glass bottles with Teflon-lined lids. Samples for inorganic chemical analyses generally shall be placed in clean polyethylene bottles. Samples for volatile organics shall be placed in septum-sealed vials. The sample bottle and cap shall be triple rinsed with the water being sampled before filling the bottle with the sample to be analyzed. Bottles for filtered samples shall be rinsed with filtered sample water and bottles for unfiltered samples shall be rinsed with unfiltered sample water. Add the appropriate preservative and cap securely. Samples must be labeled in accordance with Section 6.11. The sample bottle(s) shall be placed in a temperature controlled (4°C) chest immediately after sampling and delivered to the laboratory as soon as possible.

Note that the rinsing requirement specifically precludes adding preservative to bottles before they are shipped to the sampling site. The sampling team must have available the correct preservatives and must be trained in handling and dispensing the preservatives (Field Sampling Checklist, Appendix W).

6.7 SOILS

The sampling team is responsible for collecting representative samples that can be analyzed as received from the field. The Program Manager, Sampling Team Leader, and Contractor QAC must train the sampling team in the types of soils to be collected, the components of interest in the samples, and how to collect the sample that will represent the matrix of interest. Specifically, the sampling team must be trained to remove all items that are not integral components of the matrix of interest.



The Project QC Plan and Workplans must have considered appropriate sampling distributions and techniques, as described in Section 6.1. The sampling locations must have been chosen to be representative of the areas being investigated. At the time of sampling, these plans shall be followed. A large area may require collecting and compositing multiple samples into a single sample to represent the area. Individual samples may be collected and analyzed to describe the sampling points within the area.

All sampling points must be marked with a stake that is labeled with the appropriate Site Identification (Section 10.6). Prior to sampling, surface vegetation, rocks, pebbles, leaves, twigs, and debris will be cleared from the sample point to allow collection of a representative soil sample. After sampling each location, all equipment must be thoroughly cleaned to prevent cross-contamination of samples. Equipment shall be scrubbed and rinsed with distilled water or USATHAMA approved water, as described in Section 6.5.

Soil samples taken from borings shall be obtained via a split or solid barrel sampler (e.g., Split-Spoon, Dennison, Pitcher), or sampler equipped with a polybutyrate (or similar) liner. Borings shall be produced in a manner that preserves sample integrity and composition. Upon reaching the surface, the sampler shall be opened and the sample extracted, peeled, and bottled in the shortest time possible or, in the case of the polybutyrate liner, ends shall be capped and taped with the liner kept in a cooler at 4°C until shipping. Detailed instruction on the handling of samples using these liners will be provided on a case-by-case basis. Peeling is the process that removes the portion of sample which is in direct contact with the sampler. In addition, the ends of the sample are removed and discarded. Samples for volatiles analysis shall be peeled, bottled, and capped within 15 seconds from the time the sampler is opened.

Soil samples must be collected in containers that have been cleaned according to the protocols in Appendix F. Samples for organic and inorganic chemical analytes shall be placed in clean, wide-mouth, amber-glass bottles with Teflon-lined lids. Samples for volatiles organics shall be placed in containers appropriate for the analytical method (Section 6.4.3). Samples must be labeled in accordance with Section 6.11. Sample bottles shall be placed in a temperature controlled (4°C) chest immediately after sampling and delivered to the laboratory as soon as possible.

6.8 SEDIMENTS

The sampling team is responsible for collecting representative samples that can be analyzed as received from the field. The Program Manager, Sampling Team Leader, and Contractor QAC must instruct the sampling team in the types of sediments to be collected, the components of interest in the sample, and how to collect the sample that will represent the matrix of interest. Specifically, the sampling team must be trained to remove all items that are not integral components of the matrix of interest.



The type of sampler to be used will be dictated by the nature, as well as the accessibility, of the sediments. In addition, the type of sampler chosen should be appropriate for obtaining the desired sample, e.g., a core sampler should not be used to obtain top sediment. The Project QC Plan and Workplans should have designated appropriate sampling techniques, as described in Section 6.1. At the time of sampling, these plans must be followed.

Prior to sampling sediments in a stream, the sampling device shall be rinsed with stream water at a point downstream from the sampling location to avoid disturbing the sediments at the sampling point. Also, sampling shall be accomplished upstream of any disturbances in the stream caused by the sampler or sampling team. Twigs, leaves, pebbles, and debris that are not integral components of the matrix of interest must be removed by the sampling team.

Prior to sampling sediments in a pond or lagoon, the sampling device shall be rinsed with water near the sampling point. However, caution must be exercised to avoid disturbing the sediments at the sampling point by the rinsing activities.

After sampling each location, all equipment must be thoroughly cleaned to prevent cross contamination of samples. Equipment shall be scrubbed and rinsed with distilled water or USATHAMA-approved water, as described in Section 6.5.

Sediment samples must be collected in containers that have been cleaned according to the protocols in Appendix F. Samples for organic and inorganic chemical analytes shall be placed in clean, wide-mouth, amber-glass bottles with Teflon-lined lids. Samples for volatile organics shall be placed in containers appropriate for the analytical method (Section 6.4.3). Samples must be labeled in accordance with Section 6.11. Sample bottles shall be placed in a temperature controlled (4°C) chest immediately after sampling and delivered to the laboratory as soon as possible.

6.9 SAMPLE PRESERVATION

The purpose of sample preservation is to prevent or retard the degradation/modification of chemicals in samples during transit and storage. Efforts to preserve the integrity of the samples shall be initiated at the time of sampling and will continue until analyses are performed. Preservatives shall be added to the sample container at the time of sample collection. The recommended procedure for accomplishing this is to take premeasured volumes of the preservatives in sealed ampules to the field. Preservation and storage requirements are provided in Appendix H. Sample holding time requirements apply to all samples. Holding times begin on sampling date and not the date samples are received in the laboratory. Freezing samples to extend holding times shall not be permitted.

Sample storage shall only be terminated after all analytical results have been validated to level 3 in the USATHAMA Data Management System and approved by the USATHAMA Project



Officer. Samples may be required to be held in storage longer to fulfill contractual requirements or as directed by the USATHAMA Project Officer.

6.10 STANDING OPERATING PROCEDURES - FIELD

The organization shall have written SOPs for all field procedures and methods; all procedures shall be performed as described in the SOP. Any modification of an SOP made during a data collection activity must be documented and approved by the USATHAMA Chemistry Branch. SOPs shall be prepared for, but not limited to, the following areas:

- Sample management;
- Sample team training and documentation;
- Numbering and labelling;
- Sample tracking;
- Sample containers;
- Sample preservation and storage;
- Holding times;
- Shipping;
- Decontamination;
- Sample collection procedures;
- Corrective actions;
- Records management;
- Chemical and sample disposal; and
- Reporting.

In addition, where analyses are performed in the field, the following additional SOPs are required:

- Reagent/standard preparation and validation;



- Equipment calibration and maintenance;
- Field analysis; and
- Data reduction and validation.

A description of the basic information required in each of the above SOPs is included in Appendix G. The organization's SOP is not required to conform to a specific format but shall be representative of standard field and laboratory operations, and shall give clear evidence of the organization's ability to successfully fulfill all contract requirements.

6.11 SAMPLING

6.11.1 FIELD CHAIN-OF-CUSTODY

The necessity of having established procedures for documenting activities in the field also requires that each sample taken be delivered to the laboratory. To alleviate potential problems, the field sampling team must adequately document and identify each sample taken. This process ensures the laboratory that each sample is analyzed for the requested parameters; each sample requested is actually received at the laboratory. It is imperative that written procedures be not only available but followed, to ensure that an accurate record of sample collection and transfer activity is maintained. Chain-of-custody procedures are contained in Section 7.0.

A sample is considered to be in someone's custody if:

- It is in one's actual possession;
- It is in one's view, immediately after being in one's possession;
- It has been placed in a larger container (i.e., cooler, etc.) which remains in view, after being in someone's possession;
- It has been placed in a secured area, restricted to authorized personnel only.

6.11.2 SAMPLE HANDLING

It is important to good custody procedures that all samples be handled by a minimum number of persons. Field records must be completed at the time a sample is collected and should include the following information as a minimum.



- Project or installation for which the sample is being taken;
- Sample date and time;
- Sample location (bore or well i.d.) or source;
- Field sample number, unique to each container, if several analytical samples are being taken from the same source;
- Required analyses for each container;
- Preservative used, if any;
- Field data applicable to the sample (i.e., pH, conductivity); and
- Sampler's name.

Additional information which is required for certain samples would include:

- Sample depth, measured from the top of the well casing for established wells, and from ground level for bores; and
- Sample technique.

Information which is entered on the field chain of custody must match exactly information from the field sampling log. All entries must be made in blue or black ink, and must be legible. There shall be sufficient matching information on each sample label to verify each sample against the chain of custody. As a minimum, the following information is required:

- Sample date and time;
- Sample location (bore or well i.d.) or source;
- Field sample number, unique to each container, if several analytical samples are being taken from the same source;
- Required analyses for each container;
- Preservative used, if any; and
- Sampler's name or initials.

Unused bottles, containers, and coolers which have been shipped to a sampling location are to be kept in a secured location to minimize tampering and possible contamination. Containers



which are returned unused to a laboratory are still required to be kept under chain of custody.

When samples are to be transferred, the custodian must sign and date the chain-of-custody form(s), as must the recipient who now becomes the sample custodian. Transfers must account for each individual sample, although samples may be transferred as a group.

Mailed packages are considered under chain-of-custody if the carrier signs a form indicative of receipt; a receipt is also generated by delivery of the samples. This receipt is attached to the original chain-of-custody forms, which may be shipped inside of the cooler or container to prevent loss upon transfer. Custody seals should be placed across all openings upon shipment to ensure no tampering has occurred.

6.12 USATHAMA SAMPLE IDENTIFICATION NUMBERS

The reporting of analytical results to the USATHAMA IRDMS requires that each sample aliquot be assigned a unique six character identification number. The first three characters of this number are alpha characters that represent the analytical lot. Each analytical lot is given a different series of alpha characters. For instance a group of water samples for Metals analyses by ICP could be assigned the alpha designation of AAA. While another group of samples that contain samples for Anion analyses, some to be done by Technicon and others to be done by IC, would be given two different alpha designations. The Technicon analyses could be given a designation such as AAB and the IC analyses could be given a designation such as AAC. In the case of a multi-analyte method, the alpha designator assigned will be the same for each analyte in a single sample aliquot.

The last three characters are numeric characters that represent the individual samples within the lot. The lot size has to be determined before these numbers can be assigned. The lot size is defined as the number of samples that can be extracted, analyzed, or digested in a single day as controlled by the rate limiting step in the particular method. When USATHAMA approves a particular method during the certification process, it also approves a lot size. In Section II.E of the method's Standing Operating Procedure, the lot size is stated.

If the contractor laboratory uses an internal numbering system a correlation of the internal lab sample number to the USATHAMA lot number shall be provided in a bound logbook.



An example of the USATHAMA sample identification number assignments are provided below:

(1) Four samples are received by a particular laboratory for 2,4,6-Trinitrotoluene (2,4,6TNT), 2,4-dinitrotoluene (24DNT), trichloroethylene (TRCLE) and tetrachloroethylene (TCLEE) analyses. 246TNT and 24DNT are analyzed simultaneously with the same method; TRCLE and TCLEE are analyzed simultaneously with a different method. For this laboratory, each method (Class IB) has a maximum lot size of 8 samples. Therefore, the assignments could be made as shown in Table 6-1.

(2) For metals determination by graphite furnace atomic absorption, each metal in the set of samples must be assigned a unique lot even though the analysis may be performed using the same method and digestate. For example, six samples and their associated QC samples could be given the lot designation of ZAA for copper, ZAB for lead, and ZAC for zinc.

Table 6-1. USATHAMA LOT NUMBER ASSIGNMENT

	246TNT	24DNT	TRCLE	TCLEE
Blank	AAA 001	AAA 001	AAB 001	AAB 001
Spike(High)	AAA 002	AAA 002	AAB 002	AAB 002
Sample 1	AAA 003	AAA 003	AAB 003	AAB 003
Sample 2	AAA 004	AAA 004	AAB 004	AAB 004
Sample 3	AAA 005	AAA 005	AAB 005	AAB 005
Sample 4	AAA 006	AAA 006	AAB 006	AAB 006

Note that the analytes by the same method have the exact same sample number. Sample number sequence does not have to be in sequence as shown here.



7.0 CHAIN-OF-CUSTODY PROCEDURES

The material presented here briefly summarizes the major aspects of chain-of-custody. Reference should be made to NEIC Policies and Procedures (EPA-300/9-78-001-R) for more information.

7.1 INTRODUCTION

As in any other activity that may be used to support litigation, government agencies must be able to provide the chain-of-possession and custody of any samples which are offered for evidence or which form the basis of analytical test results introduced into evidence in any legal proceeding. It is imperative that written procedures be available and followed whenever evidence samples are collected, transferred, stored, analyzed, or destroyed. The primary objective of these procedures is to create an accurate written record which can be used to trace the possession and handling of the sample from the moment of its collection through analysis and its introduction as evidence.

A sample is in someone's "custody" if:

- It is in one's actual physical possession;
- It is in one's view, after being in one's physical possession;
- It is in one's physical possession and then locked up so that no one can tamper with it;
or
- It is kept in a secured area, restricted to authorized personnel only.

7.2 SURVEY PLANNING AND PREPARATION

The evidence-gathering portion of a survey should be characterized by the minimum number of samples required to give a fair representation of the sampled area or matrix. To the greatest extent possible, the number of samples and sampling locations should be determined prior to the survey.



All survey participants will receive a copy of the survey study plan and will be knowledgeable of its contents prior to the survey. A pre-survey briefing will be held to re-appraise all participants of the survey objectives, sample locations, and chain-of-custody procedures. After all chain-of-custody samples are collected, a debriefing will be held in the field to determine adherence to custody procedures and whether additional evidentiary samples are required.

7.3 SAMPLE COLLECTION, HANDLING, AND IDENTIFICATION

It is important that a minimum number of persons be involved in sample collection and handling. Standard field sampling techniques, such as those published by the U.S. Environmental Protection Agency, should be used for sample collection, preservation, and handling. Field records should be completed at the time the sample is collected and should be signed or initialed, including the date and time, by the sample collector(s). Field records should contain the following information:

- Unique sample or log number;
- Date and time;
- Source of sample (including name, location, and sample type);
- Preservative used;
- Analyses required;
- Name of collector(s);
- Pertinent field data (pH, temperature, depth to water, etc.); and
- Serial number of custody seals and transportation cases.

Each sample is identified by affixing a pressure sensitive gummed label or standardized tag on the container(s). This label should contain the sample identification number, date and time of sample collection, source of sample, preservative used, and the collector's initials. Analyses required should be identified. Where a label is not available, the same information should be affixed to the sample container with an indelible, water-proof marking pen.

The sample container should then be placed in a transportation case along with the chain-of-custody record form, pertinent field records, and analyses request form as needed. The transportation case should then be sealed and labeled. All records should be filled out legibly in pen.



The use of the locked and sealed chests may never eliminate the need for close control of individual sample containers. Therefore, the sampler should place a custody seal around the cap of the individual sample container which would indicate tampering if removed. In addition, all openings on the chest will be sealed with evidence tape.

When samples are composited over a time period, unsealed samples can be transferred from one crew to the next crew. A list of samples will be made by the transferring crew and signed for by a member of the receiving crew. They will either transfer the samples to another crew or deliver them to laboratory personnel who will then acknowledge receipt in a similar manner.

Color slides or photographs taken of the sample location and of any visible pollution are recommended to facilitate identification and later recollection by the sampler. A photograph log should be made at the time the photo is taken so that this information can be written later on the back of the photo or in the margin of the slide. This log should include the signature of the photographer, time, date, site location, and brief description of the subject of the photograph. Photographs and written records, which may be used as evidence, should be handled in such a way that chain-of-custody can be established.

7.4 TRANSFER OF CUSTODY AND SHIPMENT

When transferring the possession of the samples, the transferee must sign and record the date and time on the chain-of-custody record. Custody transfers, if made to a sample custodian in the field, should account for each individual sample, although samples may be transferred as a group. Every person who takes custody must fill in the appropriate section of the Chain-of-Custody Record. To prevent undue proliferation of custody records, the number of custodians in the chain-of-possession should be as few as possible.

The field custodian, or field inspector if a custodian has not been assigned, is responsible for properly packaging and dispatching samples to the appropriate laboratory for analysis. This responsibility includes filling out, dating, and signing the appropriate portions of the Chain-of-Custody Record. A Chain-of-Custody Record format, containing the necessary procedural elements, is shown in Figure 7-1.

All packages sent to the laboratory should be accompanied by the Chain-of-Custody Record and other pertinent forms. A copy of these forms should be retained by the originating office (either carbon or photographic copy).



Figure 7-1. Sample Chain of Custody Record

[illegible]

8-0921

Mailed packages can be registered with return receipt requested. If packages are sent by common carrier, receipts should be retained as part of the permanent chain-of-custody documentation. Any other commercial carrier transmittal documents shall also be maintained with the permanent chain-of-custody documentation.

Samples to be shipped must be so packed as not to break and the package so sealed or locked that any evidence of tampering may be readily detected. Custody seals are narrow strips of adhesive paper used to demonstrate that no tempering has occurred. They are intended for use on a sample transport container and for routine use on individual sample containers.

7.5 LABORATORY CUSTODY PROCEDURES

Chain-of-custody procedures are also necessary in the laboratory from the time of sample receipt to the time the sample is discarded. The following procedures are recommended for the laboratory:

- A specific person shall be designated custodian and an alternate designated to act as custodian in the custodian's absence. All incoming samples shall be received by the custodian, who shall indicate receipt by signing the accompanying custody forms and who shall retain the signed forms as permanent records.
- The sample custodian shall maintain a permanent log book to record, for each sample, the person delivering the sample, the person receiving the sample, the date and time received, the source of the sample, the sample identification or log number, how the sample was transmitted to the laboratory, and the condition received (sealed, unsealed, broken container, or other pertinent remarks). A standardized format should be established for log book entries. A sample receipt checklist (Appendix S) shall be used by the sample custodian as an aid in logging in the samples. A copy of the checklist shall be incorporated into the lot data package.
- A clean, dry, isolation room, building, and/or refrigerated space that can be securely locked from the outside shall be designated as a "Sample Storage Security Area."
- The custodian shall ensure that heat-sensitive, light-sensitive, radioactive, or other samples having unusual physical characteristics or requiring special handling, are properly stored and maintained prior to analysis.



- Distribution of samples to individuals who are responsible for the laboratory performing the analysis shall be made only by the custodian.
- Laboratory personnel are responsible for the care and custody of the sample once it is received by them and shall be prepared to testify that the sample was in their possession and view or secured in the laboratory at all times from the moment it was received from the custodian until the time that the analyses were completed.
- Once the sample analyses are completed, the unused portion of the sample, together with all identifying labels, must be returned to the custodian. The returned tagged sample should be retained in the custody room until permission to destroy the sample is received by the custodian.
- Samples shall be destroyed only after all analytical results have been validated to level 3 in the USATHAMA Data Management System and such action is approved by the USATHAMA Project Officer. Samples may be required to be held in storage longer to fulfill contractual requirements or as directed by the USATHAMA Project Officer.

7.6 QUESTIONS/PROBLEMS CONCERNING CUSTODY RECORDS

If a discrepancy between sample tag numbers and custody record listing is found, the person receiving custody should document this and properly store the samples. The samples should not be analyzed until the problem is resolved.

The responsible person receiving custody should attempt to resolve the problem by checking all available information (other markings or sample container, type of sample, etc.). He should then document the situation on the custody record and in his project log book and notify the project manager and quality control coordinator by the fastest available means, followed by written notification.

Changes may be written in the "Remarks" section of the custody record and should be initialed and dated. A copy of this record should accompany the written notification to the project manager and quality control coordinator.

7.7 EVIDENTIARY CONSIDERATIONS

Reducing chain-of-custody procedures as well as the various promulgated laboratory analytical procedures to writing will facilitate the admission of evidence under Rule 803(6) of the



Federal Rules of Evidence (PL 93-575). Under this statute, written records of regularly conducted business activities may be introduced into evidence as an exception to the "Hearsay Rule" without the testimony of the person(s) who made the record. Although preferable, it is not always possible to have the individuals who collected, kept, and analyzed samples testify in court. In addition, if the opposing party does not intend to contest the integrity of the sample or testing evidence, admission under Rule 803(6) can save a great deal of trial time. For these reasons, it is important that the procedures following in the collection and analyses of evidentiary samples be standardized and described in an instruction manual which, if need be, can be offered as evidence of the "regularly conducted business activity" followed by the laboratory or office generating any given record.

If evidence is to be used in criminal actions, special conditions apply to use of the "Hearsay Rule." It is arguable that those portions of a sampling and analysis report dealing with matters other than sampling and analysis results come within this exception. In criminal actions, records and reports of matter observed by field investigators may not be admissible and the evidence may still have to be presented in the form of oral testimony by the person(s) who made the record or report, even though the materials come within the definition of business records. In a criminal proceeding, the opposing counsel may be able to obtain copies of reports prepared by witnesses, even if the witness does not refer to the records while testifying, and if obtained, the records may be used for cross-examination purposes.

Admission of records is not automatic under either of these sections. The business records section authorizes admission "unless the source of information or the method or circumstances or preparation indicate lack of trustworthiness," and the caveat under the public records exception reads "unless the source of information or other circumstances indicate lack of trustworthiness."





8.0 CALIBRATION PROCEDURES AND FREQUENCY

8.1 CHEMICAL CALIBRATION CURVES

Before samples are analyzed on an instrument, chemical calibration standards of each target analyte must be analyzed to establish that the instrument is functioning properly with the desired sensitivity. Economy of effort dictates that as many analytes as possible be combined in the chemical calibration standards.

Chemical instrument calibration will be accomplished using calibration standards prepared by mixing the species to be analyzed in the solvent that is introduced into the instrument, as dictated by the analytical method. The concentrations of the chemical calibration standards will be chosen to bracket the certified range of the method. That is, at least one calibration standard will have a concentration 10 percent less than the CRL and at least one calibration standard will have a concentration 10 percent greater than the upper certified limit.

Data from the chemical calibration standards will be plotted, only during the precertification/certification process, or as necessary, with the instrument response indicated on the ordinate and the concentration indicated on the abscissa. When microprocessors are used to establish calibration curves, the data must nevertheless be plotted. If, after plotting, the curve is shown to be linear with acceptable variance, the microprocessor may be used to determine analyte concentrations in samples. Methods and formulae for quantification will be specified in the standardized methods.

Chemical instrument calibration curves may not be used to determine the method CRL. Rather, analysis of chemical calibration standards are to be used by instrument operators to establish response versus concentration relationships and to provide early warning of instrument variances.

For Class 1, Class 1A, or Class 1B multi-analyte methods, if at least 2/3 of the analytes pass calibration, by required percentage or two standard deviations, the method is considered to be in control.

Numbers and concentrations of standards to be analyzed during calibrations performed for different ranges (linear and Zero-Intercept (ZI)) and different certification classes are summarized in Table 8-1.

Data from the calibration checks are to be recorded on forms (Appendix V) and maintained with the lot data package. Alternatively, if a laboratory-wide computerized data management system is available, data calibration may be generated electronically and output on forms or charts. In either case, documentation must be available to demonstrate the validity of the calibration checks.



8.1.1 INITIAL CALIBRATION, CLASS 1, CLASS 1A, AND CLASS 1B METHODS

Initial Calibration procedures shall be used whenever:

- The first day of certification analyses 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.

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 (using approximately the same concentrations as the precertification calibration standards, Section 5.3) shall be analyzed singularly on one day. The concentrations of the calibration standards, in the solvent that results from all the preparation steps of the method, shall take into account any concentration steps that are part of the method. That is, if the resulting certified range of a method is from 10 ug/L to 100 ug/L, and the method incorporates a ten fold concentration, then the calibration standards must span and bracket the range from 100 ug/L to 1000 ug/L. Concentrations in the solvent shall correspond to those in an environmental matrix as if the method preparation steps had been performed. For example, if the environmental sample concentration were 10 ug/L and a 100-fold concentration occurs during sample preparation, the corresponding calibration standard concentration is 1,000 ug/L. If the tested range is extended by adding certification samples, the same number of additional calibration standards shall be included.

In addition to the initial calibration standards, Class 1 and 1B methods require the analysis of calibration check standards (Section 8.2). During a Class 1 or Class 1B initial calibration, a calibration check standard shall be 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 to be analyzed once a week rather than each day. The concentration of the calibration check standard shall be near the upper end of the certified range and shall contain all the analytes of interest. Calibration check standard results shall be within the limits of acceptability defined in Section 8.2. For multi-analyte methods at least 2/3 of the analytes must be within the limits of acceptability (see Table 11-2). In addition, the results are not acceptable if the same analyte is outside the limits of acceptability in two consecutive calibration check standards.



Table 8-1. NUMBERS AND CONCENTRATIONS OF CALIBRATION STANDARDS
(LINEAR AND ZERO-INTERCEPT)

PRECERTIFICATION - CLASS 1

Minimum Testing Range (MTR): 12 Standards + 1 Check Standard (CS)

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 (Section 5.3)



Table 8-1 (cont) NUMBERS AND CONCENTRATIONS OF CALIBRATION STANDARDS
(LINEAR AND ZERO-INTERCEPT)

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 : 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 : 4 Standards

Blank and 1 TRL (Duplicate)



- * 10 percent to 25 percent Range Extension (Section 5.3)
Table 8-1 (cont) NUMBERS AND CONCENTRATIONS OF CALIBRATION STANDARDS
(LINEAR AND ZERO-INTERCEPT)

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 : 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



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: 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: 4 Daily

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 shall be halted and shall not resume until successful completion of initial calibration. Corrective action taken to restore initial calibration shall be documented by the contractor laboratory.

8.1.2 DAILY CALIBRATION, CLASS 1, CLASS 1A, AND CLASS 1B METHODS

Calibration standards shall be analyzed each day to verify that instrument response has not changed from previous calibration. Before sample analysis each day (ZI Model only), the highest concentration standard shall be 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 shall be reanalyzed. If the response from the second analysis is not within the required percentage or two standard deviations of the mean response from precertification, certification, and prior Initial/Daily Calibrations, Initial Calibration must be performed before analyzing samples.

After sample analyses are completed each day (ZI Model only), the highest concentration standard shall be 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 is not within the required percentage or two standard deviations of the mean response from precertification, certification, and prior Initial/Daily Calibrations, the system is considered to have failed calibration. Initial Calibration must be performed and all samples analyzed since the last acceptable calibration must be reanalyzed.

For non-linear or non-ZI calibration curves, Daily Calibration shall consist of analysis of the low, middle, and high calibration standards at the beginning of the day. When sample analysis are completed at the end of the day, the low and high standards shall be 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 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 LOF are required, as a minimum.

8.1.3 INITIAL CALIBRATION, CLASS 2 METHODS

The instances when Initial Calibration must be performed are the same as described in Section 6.5.1. Calibrations standards shall be prepared and analyzed in triplicate at concentrations of 0 (blank) and the CRL (TRL prior to or during certification). The spiked concentration shall correspond to the CRL in the environmental matrix. All blanks must yield negative results and all spiked samples must yield positive results for acceptable calibration.

8.1.4 DAILY CALIBRATION, CLASS 2 METHODS

Before and after sample analysis each day, one blank and one calibration standard at the CRL shall be analyzed. If any calibration standard yields an inappropriate response (positive for a blank, or negative for the spiked standard), a second calibration standard shall be analyzed. If the second standard yields an inappropriate response, the system is considered to have failed calibration. The cause of the failure must be determined and corrected before analyses may continue.

If calibration failure occurs at the end of sample analyses, the analytical results obtained since the last satisfactory calibration are considered invalid and must be repeated. After calibration failure, the procedure for the Initial Calibration must be followed to demonstrate satisfactory performance.



SECTION 8.2 CALIBRATION CHECK STANDARDS

SECTION 8.2.1 REQUIREMENTS FOR USE

Calibration check standards are required for all Class 1 and 1B methods and shall be analyzed during precertification and with each initial certification. The calibration check standard shall contain 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 in Section 8.2.2.

SECTION 8.2.2 LIMITS OF ACCEPTABILITY

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 shall be $\pm$ two standard deviations, as determined from the first seven points.



SECTION 8.2.3 MULTI-ANALYTE METHODS

For multi-analyte methods, the calibration check standard shall contain 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 defined in Section 8.2.2 (see Table 11-2). In addition, if a single analyte falls outside the limits of acceptability for two consecutive times, then the calibration check standards is deemed unacceptable. If a calibration check standard is not acceptable the contractor laboratory shall follow the procedures detailed in Section 5.3 and 8.1.1.

8.3 REFERENCE MATERIAL

During certification, chemical calibration, and sample analyses, solutions containing known analytes at known concentrations must be prepared. These solutions are needed to generate certification data, calibrate instruments, spike analytical surrogates or internal standards, prepare QC samples, and prepare performance samples, when specified. Three types of reference materials may be used to prepare standard solutions, as described in Sections 8.3.1 through 8.3.3.

Before initiating any laboratory studies, the Contractor Laboratory must submit a request to the USATHAMA Project Officer or Contracting Officer's Representative for reference materials. The list should include all target analytes of interest on a specific project, surrogate compounds, and internal standards. The USATHAMA Project Officer or Contracting Officer's Representative will forward the request to the USATHAMA Chemistry Branch. Samples of reference materials will be shipped to the Contractor Laboratory from the repository. Only if reference materials are not available through USATHAMA should the Contractor Laboratory obtain the materials from an outside source.

Reference materials for metals and non-metallic inorganics may be maintained at room temperature in a locked storage area. All other reference materials must be stored in a locked refrigerator at or below 4°C. All reference materials shall be maintained under chain-of-custody. An SOP for the use, control, and inventory of reference materials will be prepared.

8.3.1 STANDARD ANALYTICAL REFERENCE MATERIALS (SARMs)

Whenever possible, chemical analyses conducted in support of USATHAMA IR projects should be based on SARMs. These materials are labeled as SARMs and carry a SARM identification number. These materials will either be National Institute of Standards and Technology (NIST) Standard Reference Materials (SRMs) or will be traceable to NIST SRMs. The SARM Repository Program is described in Appendix I. Contractors are encouraged to use secondary standards that are referenced to SARMs and are periodically checked against



SARMs. This check will be performed the first time the standard is used and at six month intervals or when the standard is replaced, whichever comes first.

The use of secondary standards are encouraged as a conservation method for the more costly SARMs.

8.3.2 INTERIM REFERENCE MATERIALS (IRMs)

IRMs are available from two sources. Some of these materials are maintained and distributed by USATHAMA and should be used if SARMs are not available. Although IRMs are supplied through USATHAMA, they are not as rigorously characterized, as are SARMs. IRM characterization includes positive identification of the material and an estimate of purity. The SARM label on each bottle is modified by adding the word "Interim" and includes an identification number. These materials may be used as received from USATHAMA. Reference materials obtained from the U.S. Environmental Protection Agency, or NIST do not require characterization by the Contractor Laboratory.

8.3.3 OFF-THE-SHELF MATERIALS

SARMs or IRMs may not be available for some target analytes. If materials are unavailable through USATHAMA, Contractor Laboratories will be instructed to purchase materials from an outside supplier. Before using any material, regardless of source, classified as "off-the-shelf," the Contractor Laboratory must analyze the material to obtain a positive identification and estimate of purity. Where possible, characterization analyses for purity shall be conducted using at least two different methods. Off-the-shelf materials should be compared to NIST or EPA standard material whenever possible. The characterization analyses must be performed before certification efforts are initiated and the results must be provided to USATHAMA with the Precertification Performance Data Package. Documentation for purity and identity characterization analyses shall be kept on file at the contractor laboratory. Possible techniques for characterizing the off-the-shelf materials include, as applicable:

- Infrared spectroscopy;
- Melting point, decomposition point, or boiling point determinations;
- Mass spectrometry;
- NMR spectrometry;
- Elemental analysis;
- Gas chromatography (for purity); or



- Liquid chromatography (for purity).

This list is not exhaustive and all of the listed techniques need not be used. The Contractor Laboratory is responsible for providing positive identification and a purity estimate for each off-the-shelf material (including internal standards) to USATHAMA with the Precertification Performance Data Package (Section 14.3).





9.0 SAMPLE ANALYSIS

9.1 STANDING OPERATING PROCEDURES - LABORATORY

The laboratory shall have written SOPs for all procedures and methods, including sample analysis, laboratory functions, and auxiliary functions, prior to the analysis of field samples. Procedures and methods shall be performed in the laboratory as described in the SOP. Any modification of an SOP made during a data collection activity must be documented and approved by the USATHAMA Chemistry Branch. SOPs shall be prepared for, but not limited to, the following areas:

- Sample receipt and logging;
- Laboratory personnel training and documentation;
- Sample and extract storage;
- Sample scheduling;
- Preventing sample contamination;
- Security for laboratory, samples, SARMS, and standard soil;
- Traceability/Equivalency of standards;
- Standard solution verification;
- Maintaining instrument records and logbooks;
- Sample analysis and data control systems;
- Glassware cleaning;
- Technical and managerial review of laboratory operation and data package preparation;
- Internal review of contractually-required quality assurance and quality control data for each individual data package;
- Sample analysis, data handling and reporting;
- Data reduction and validation;



- Chain of custody;
- Document control, including data package preparation;
- Corrective actions; and
- Records management.

A description of the basic information required in each of the above SOPs is included in Appendix J. The laboratory SOP is not required to conform to a specific format but shall be representative of standard laboratory operations, and shall give clear evidence of the laboratory's ability to successfully fulfill all contract requirements.

9.2 SAMPLE HOLDING

The time that a preserved sample may be held between sampling and analysis is based on the analyte(s) of interest. Holding time limitations are intended to minimize chemical change in a sample before it is analyzed. The holding time is the maximum time allowable between sample collection and the completion of analysis, based on stability factors. The holding times specified in this document do not preclude shorter analysis and reporting requirements which may be specified in the contract. Allowable holding times (Appendix H) apply to both solid and aqueous samples. Results reported for samples analyzed after holding times have been exceeded shall be considered out-of-control and unacceptable. To expedite analysis and to minimize the possibility of exceeding holding times, samples should be sent to the laboratory by a fast, reliable method, as soon as possible after collection.

9.3 SAMPLE PREPARATION/FILTRATION

Water used in the course of organic analyses shall conform to ASTM Type II grade. Water used in the course of inorganic analyses shall conform to ASTM Type I grade (Table 5-1, Section 5.6.1). Standard and QC samples for organic analyses shall conform to ASTM Type II grade with 100 mg/L sulfate and chloride added.

9.3.1 WATER SAMPLES

The need to filter water samples depends on whether total or dissolved contaminants are of interest. The project-specific decision must be explicitly stated in the Project QC Plan. Assessment objectives must be considered when specifying filtration requirements, procedures, and materials in the Project Workplan.



Samples for any dissolved constituents (organic or inorganic) must be filtered in the field if a chemical additive is used for preservation. Volatile organic compounds and oil/grease are the only universal exemptions to this guideline; samples for these two analyte classes are never filtered. Samples for dissolved metals analyses must be filtered in the field, before adding chemical preservatives, to preclude extraction of contaminants from the particulate matter by the preservatives. Samples for organic analyses generally should be filtered in the laboratory. The filter material used in the field or the laboratory must be compatible with the constituents of interest. Compatibility is defined in the following way:

- The filter material is not changed by the material being filtered (and vice versa); and
- The filter material does not absorb or leach the chemical species for which the sample will be analyzed.

The compatibility requirement may necessitate filtering individual subsamples for specific analytes if a universally compatible filter material cannot be identified. Exceptions to these guidelines must be obtained in writing from the USATHAMA Chemistry Branch.

Generally, particulate matter is not considered to be a natural component of groundwater, and groundwater samples (Section 6.5.1) will normally be filtered through a 0.45 micron filter prior to analysis; however, samples for analysis of oil and grease or volatile compounds will never be filtered. Filtration of surface water (Section 6.6), drinking supply water (Section 6.5.2), or tap water (Section 6.5.3) will be determined by specific project needs. If filtration is performed, the specifications for groundwater samples will apply.

9.3.2 SOIL/SEDIMENT SAMPLES

Soils and sediments are very complex mixtures with widely varying compositions, even within a single site. Recovery of analytes depends on many factors, including organic content, mineral content, particle size, and moisture content of the soil. Soil and sediment samples shall be analyzed in the as-received condition and prepared as follows:

- The sample shall be mixed as thoroughly as possible in the wide-mouth, amber-glass bottle by shaking and/or stirring. Glass or Teflon rods may be used for stirring (does not apply to samples for volatiles analysis).



- For each sample, an aliquot of the as-received sample shall be dried according to the procedure in ASTM D2216-71, "Laboratory Determination of Moisture Content of Soil" (Note that the calculations specified in the method do not apply; only the drying procedure itself is of interest). The calculated percent moisture for each sample shall be entered into the USATHAMA IRDMS (Section 6.7). The determination of percent moisture is calculated as follows:

$$\frac{\text{Sample Weight (wet)} - \text{Sample Weight (dry)}}{\text{Sample Weight (wet)}} \times 100$$

- The moisture determination on a sample designated for volatiles analysis shall be performed on a duplicate of the sample and not the sample itself.
- Weighed aliquots of the mixed sample shall be obtained for each analysis. All samples will be analyzed and reported in the as-received condition.

9.4 SAMPLE ANALYSIS

All samples shall be analyzed by lot. A lot is the maximum number of samples, including QC samples, that can be manually processed through the rate limiting step of the method during a single time period (not to exceed one day, 24 hours, as defined by the process). The rate of sample collection or shipment does not determine maximum lot size, although it may limit the number of samples available for analysis at a given time. A lot may consist of samples from more than one installation as long as the data quality objectives for each of the installations are the same. The rate limiting step may be determined by time or by equipment limitations. All samples in one lot must be completely processed through any given step in the same time period. For example, suppose a laboratory can extract 10 samples at one time, can concentrate 20 sample extracts at a time, and can instrumentally analyze 50 sample extracts at a time. The lot may only contain 10 samples because no more than 10 samples can be processed at one time during the rate limiting (extraction) step.

All samples must be processed through the entire analytical method, exactly as certified (Section 5.0). Any proposed modifications to the certified method must be evaluated and approved by the USATHAMA Chemistry Branch before use. All instrumental measurements must be made within the certified range (Section 5.7.1) of the method. Any samples with concentrations above the certified range must be diluted within range for concentration measurement. Records of all dilutions must be maintained and the dilution factors shall be entered into the USATHAMA IRDMS (Section 10.4). If a large number of samples require dilution, the USATHAMA Project Officer shall decide whether samples are diluted or the

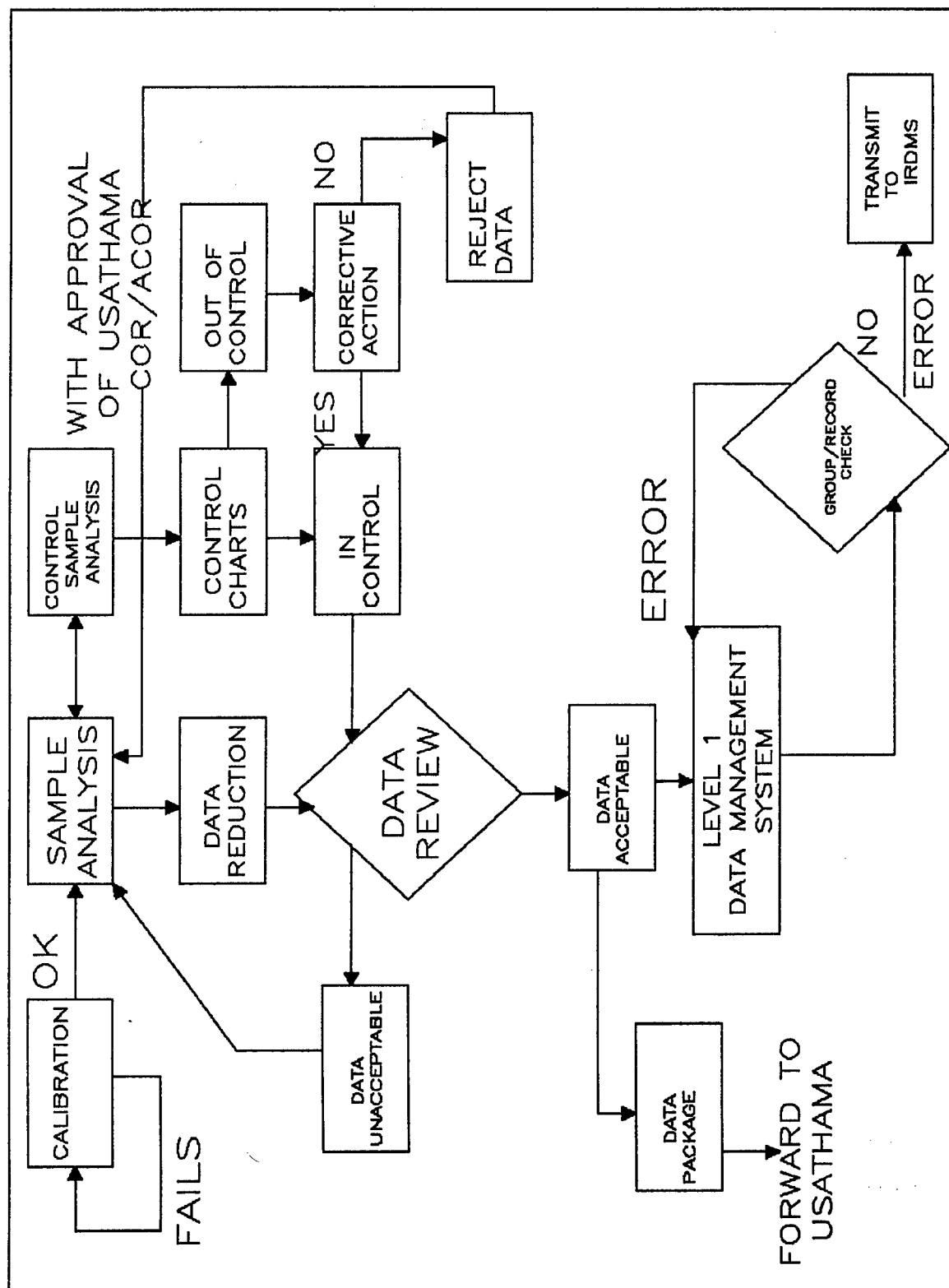


certification range is to be extended. The method of analyte identification and quantification will be specified in the analytical methods. A typical sequence of sample analysis through data transmission is shown in Figure 9-1.

In any chromatographic method, excluding GC/MS, the presence of a compound shall be confirmed (as long as confirmatory method is available) on a second column. The confirmation does not have to be through the use of a Class 1 certified method but the limitations on the method must be well documented, i.e., Class 2 certification. Confirmation does not necessarily have to be performed within holding times but must be accomplished within 10 days of sample analysis.



Figure 9-1.



10.0 DATA REDUCTION, VALIDATION, AND REPORTING

Traditionally, record keeping was the primary emphasis of QA. Although the primary emphasis of this USATHAMA QA Program is the control of sample analysis, record keeping maintains its importance in the overall assessment of the production of quality 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 will be required. In any case, the records described below shall be maintained and will be available for inspection by USATHAMA.

10.1 RECORD KEEPING

Bound logbooks with pre-numbered pages shall be utilized for record keeping. In addition to the pre-numbered pages, each logbook or laboratory notebook shall have a unique number for ease of identification. Additional documentation, such as chromatograms, shall be referenced to the logbook or notebook, where appropriate. Loose sheets are not to be used unless permanently affixed to the logbook. The use of bound books tends to result in a chronological sequence of data insertion. Numbered pages encourages use of data in sequence and also aids in referencing data through a table of contents ordered according to time, type of analysis, type of sample, and/or identity of analyst.

Validation can be easily accomplished by requiring the sampler or analyst to date and sign each activity or analysis on the day completed. This validation can be further strengthened by providing space for the supervisor to witness the date and the completion of the analyses.

Logbook entries shall be completed in ink. Corrections should be made by drawing one line through the incorrect entry, entering the correct information, initialling, and dating the change. Complete information should be entered so that in an examination it can be determined what was done, by whom, when, and what the results were. At the end of each day, the analyst will sign after the last entry is made.



Computerized logging systems may be used as support tools during any record keeping activities. However, bound logbooks are required for original records. If computers are used, bound logbooks must nevertheless be maintained. A computer hardcopy that has been permanently affixed in the logbook is acceptable as an original record of sampling and laboratory logging.

Separate installation logbooks or partial logbooks in other formats (e.g., analytical lot) maintained in conjunction with the installation logbook are the preferred methods for documenting appropriate information relevant to chemical analyses performed during USATHAMA projects. Master instrument logbooks are acceptable; however, such logbooks generally remain permanent property of the laboratory. Whatever logbook practice is utilized should minimize the duplication of records and be identified in the project QC plan submitted to USATHAMA. Logging, tuning, calibration, and reporting activities must be included in the logbooks. Copies of laboratory notebooks that integrate all projects shall not be acceptable. Routine maintenance activities (Chapter 13) do not require installation-specific logbooks.

At the end of a project, all logbooks containing information specific to the installation shall be forwarded to USATHAMA for maintenance. Corporate controlled logbooks should be avoided; however, if such logbooks are used by the laboratory, certified copies of all relevant logbook pages shall be submitted to USATHAMA. A certified copy is a copy with the source documented, signed, and dated, after copying, by the Laboratory Task Manager or Quality Assurance Coordinator.

Because exact procedures vary between laboratories, an exact system for documentation will not be specified. However, the records described in the following sections must be maintained for each USATHAMA project.

10.2 LABORATORY

10.2.1 LABORATORY LOGGING

Upon arrival at the laboratory, samples shall be logged into a bound laboratory book, preferably installation specific. Logging the samples into a laboratory-wide sample tracking system (logbook or computer) does not supplant the need for a written project-specific log. Sample information provided in the logbook must include:

- Field sample number;
- Date of arrival at the laboratory;
- Observations concerning the conditions under which the samples arrived, e.g., broken containers, leakage, lack of temperature control, etc;



- Analyses requested; and
- USATHAMA sample identification number (in addition to any internal laboratory sample numbers) associated with each field sample number. The USATHAMA sample identification numbers must be sequential, including laboratory QC samples, in the format described in Section 6.12.

Prior to the analysis, samples are grouped into analytical lots, ordered and assigned a USATHAMA sample identification number. The laboratory may use internal laboratory sample numbers in addition to the required USATHAMA designation. USATHAMA sample identification numbers will be assigned for the QC samples to ensure inclusion of the correct number of QC samples in each lot for each analytical method (Section 11.2.3).

10.3 ANALYTICAL RECORDS

Reference Materials:

A bound logbook record must be maintained of all reference materials (Section 6.5) used on a project. The record must include date of receipt, source, purity, all compositional information, storage conditions, and expiration date. Also include data obtained during characterization of purchased materials (Section 8.3.3).

Working standards made from reference materials must be labeled with complete information on preparation date, concentration of each compound, solvent, preparer's name, expiration date, and logbook where information on the standard is recorded. Reagents must be labeled with date received and expiration date, if applicable. All of the information described above must also be recorded in a bound logbook. Measurements made during standards preparation (e.g., from weighing operations) must also be recorded. There should be no bottle, flask, beaker, or vial that contains a sample, sample extract, or standard solution that is not correctly labeled and properly stored.

Sample Handling:

Each person conducting any part of an analytical protocol must maintain a record of all activities in a bound logbook. This notebook shall be specific to the operation but need not be person-specific if several individuals perform the same operation. Each day the analyst must record the samples handled, standards used, QC samples prepared, procedures used, and resultant calculations. The logbook must be signed and dated daily.



10.4 DATA REPORTING

All numerical results shall be reported in terms of concentration in the environmental sample. Resultant found concentrations submitted for entry into the USATHAMA IRDMS must remain unadjusted before being reported to USATHAMA. Correction factors (e.g., accuracy, percent moisture, and dilution factor) are maintained separately in the IRDMS. All data must have been collected during periods when calibration and control systems were used. As described earlier, only concentrations measured within the certified range, prior to correction, may be reported. Specific instructions are provided in the IRDMS User's Guide regarding the coding of entries. Flagging codes, as described in the IRDMS User's Guide will be used, when applicable, to comment on the usability of the data. Contractor Laboratory comments on the useability of data are mandatory.

In reporting results, rounding to the correct number of significant figures should occur only after all calculations and manipulations are completed. As many figures as are warranted by the analytical technique should be used in pre-reporting calculations. Premature rounding can significantly affect the final result.

Rounding will be accomplished using the following rules:

Rule 1 - In expressing an experimental quantity, retain no digits beyond the first uncertain one.

Rule 2 - In rounding numbers (i.e., in dropping superfluous digits);

- Increase the last retained digit by one if the residue is larger than 5;
- Retain the last digit unchanged if the residue is less than 5; and
- Retain the last digit unchanged if even, or increase it by one if odd, if the residue is exactly 5.

The correct number of reported significant figures, by certification type, are as follows:

- Class 1 and 1B - 3 significant figures;
- Class 1A - 2 significant figures; and
- Class 2 - 2 significant figures.

The number of allowable significant figures are reduced when added uncertainties are included in the analysis, i.e., the results for samples diluted into the certified range allow one



less significant figure due to the uncertainty added by the dilution process.

When required by contract or task order, data may have to be reported according to EPA CLP format, in addition to those described above.

10.4.1 CLASS 1, CLASS 1A, AND CLASS 1B CERTIFIED METHODS

All uncorrected values less than the CRL (Section 4.8.2), including no response, will be reported as "less than" the reporting limit.

Class 1 and 1B Methods:

If results for an analyte were obtained using the method exactly as tested, without dilution, the analyte concentration in the sample may be reported to three significant figures. If dilution was required for a particular analyte, the result may be reported to only two significant figures, reflecting the fact that total method performance was not demonstrated at that concentration during certification.

Class 1A Methods:

Results for certified analytes (target and surrogate) may be reported with two significant figures if the method was used without dilution. Results obtained after dilution and results of screening for non-certified analytes may be reported to only one significant figure. Any results for Class 1A methods that result from manual integration of chromatographic peaks shall be justified with copies of the specific peaks (instrument integration and manual integrations) provided in the data package.

10.4.2 CLASS 2 CERTIFIED METHODS

The results of Class 2 certified methods are not adjusted for dilution or accuracy. The results for samples analyzed by Class 2 certified methods are measured in relation to the CRL (two significant figures) and reported as "less than, equal to, or greater than" the CRL. A tested concentration range is not applicable since only the CRL concentration is tested.

10.5 DATA DELIVERABLES

In addition to those requirements of providing the results of analyses, both for analytical samples and QC samples, to the USATHAMA Data Management System, the contractor laboratory is responsible for maintaining and providing to USATHAMA the following documentation:



- Data Package - A data package contains all the data necessary to support the results of one analytical method for one lot of samples. Data packages must be "free standing," that is, all data should be available without reference to other documents or files. The data package will be forwarded to USATHAMA at the completion of the project or as otherwise specified (i.e., delivery order package or case file package). The description of the contents of a data package and the requirement for their review are contained in Section 10.5.1.
- Delivery Order Package - A delivery order package consists of all the data packages associated with a specific delivery order of a contract and will be forwarded to USATHAMA at the completion of the analyses specified in the delivery order.
- Case File - A case file consists of the data or data packages associated with a specific case as defined in the EPA Contractor Laboratory Program. When specified, data may be required to be delivered to USATHAMA following EPA CLP protocols, at the completion of the analysis of a case lot of samples.
- Other - As required in a contract or delivery order, data and/or data packages may be required to be delivered to USATHAMA at a specified frequency other than those described above.

10.5.1 DEVELOPMENT AND USAGE OF DOCUMENT CONTROL PROCEDURES

10.5.1.1. PURPOSE AND DEFINITION

Document control procedures are necessary in order to produce a litigation quality data package. A data package should contain all the data necessary to support the results of one analytical method for one lot of samples. Data packages should be "free standing," that is all data should be available without reference to other documents or files.

10.5.1.2 CONTENTS OF DATA PACKAGE

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:

- Original chromatograms, strip charts, or other instrument output.
- Original chain of custody form and carrier transmittal documents.
- All hardcopy GC/MS output.
- Expanded scale blow-up of manually integrated peak(s).
- All data sheets or other preprinted forms used by the contractor 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 list 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.

It is the responsibility of the contractor laboratory to review data packages for both content and correctness (see Section 10.5.1.3).

Included in the data package should be a discussion on the observations on the data contained in that package. This discussion shall include, but not be limited to, observed matrix effects, blank results, control problems, deviations from approved SOPs, digressions from normal practices (i.e., manual integrations) and reasons thereof, etc. The impact on the usability of the data shall be discussed. Explanations on the use of the applicable flagging codes shall be provided.

10.5.1.3 REVIEW OF DATA PACKAGES

All data packages shall be reviewed by the contractor laboratory. This review serves two primary purposes. First it ensures that all required data and documents are contained in the data package. Secondly it checks the content for record keeping errors.



Reviewer's names and dates of review should be recorded on the data package checklist. If any corrective actions are required they should also be noted. When corrective actions are completed the reviewer should place his/her initials and date next to the original comment. The responsibility for final review of all data packages resides with the Quality Assurance Officer of the contractor laboratory. The final step in any evaluation shall be the attesting, in writing, of the Quality Assurance Coordinator as to the validity and usability of the data.

Additional reviews are performed at USATHAMA after receipt of the data packages. Specific procedures for the reviews are covered in USATHAMA Chemistry Branch internal SOPs.

10.5.1.4 NOTEBOOKS

All contractor laboratories are required to use bound notebooks. Both the sewn binding and the plastic binding (i.e., 19 ring GBC plastic binders) are acceptable. Pages shall be pre-numbered prior to use. Each notebook should be assigned a unique notebook number which should be recorded on the cover and on each page of the notebook.

Each page shall be signed and dated by the analyst and supervisor. Corrections should be made by drawing a single line through the incorrect entry. Each correction should be initialed and dated and also include a brief explanation for the correction. The use of correction media is prohibited.

If material is copied for inclusion in the notebook, the copy must be legible and not reduced to an excessive degree.

10.5.1.5 FORMS

If the contractor laboratory uses preprinted forms for recording of data, then the original must be placed into the data package and a copy retained in the appropriate notebook.

Forms should be designed to be specific to a given analysis. All spaces should be filled, either with the required data or with a N/A to signify that the item is "not applicable" to the analysis.

Corrections should be made with a single line through the incorrect entry, initialed, dated, and with a short explanation. The use of correction media is prohibited.

10.6 DATA MANAGEMENT SYSTEM

The results for samples analyzed in support of USATHAMA projects must be entered in the USATHAMA IRDMS. Specific instructions for format, coding, and submission are provided in



the IRDMS User's Guide. In order to facilitate correct and efficient data submission, the information listed in the IRDMS User's Guide should be collected, recorded, and provided to contractor data management personnel. Questions pertaining to data management should be referred to the contractor data management group. Laboratories are encouraged to interface their internal data management system (i.e., LIMS) to the IRDMS. USATHAMA will provide assistance in the accomplishment of that interface. A typical sequence of Data Management activities are shown in Figure 10-1. Any problems with USATHAMA provided software shall immediately be reported to the USATHAMA Chemistry Branch. Direct contact with the Data Management Contractor is discouraged.

Laboratories are required to perform group and record checks of the data before transmission to the USATHAMA IRDMS. Any errors that can be corrected by the laboratory must be corrected before transmission; otherwise the data will be returned unprocessed. Data that cannot be corrected by the laboratory, e.g., results outside certified range, will be reviewed by the USATHAMA Chemistry Branch for acceptance into the IRDMS.

10.7 DATA REPORTING FOR GC/MS NON-CERTIFIED COMPOUNDS

The following procedure provides a standard format for the reporting of data for gas chromatography/mass spectrometry (GC/MS) non-certified compounds. This procedure is to be followed by all laboratories reporting data to the USATHAMA IRDMS:

- The "detection limit" (certified reporting limit) for non-certified compounds are adapted from the EPA Contract Laboratory Program's Required Quantitation Limits and are defined in Appendix X. The level appropriate to the method being used should be selected.
- If a non-certified compound is detected at or above the detection limit, it will be entered into the IRDMS using the compound test name, the calculated value, and a flagging code of "S."
- If a non-certified compound is not detected the data will be entered into the IRDMS using the compound test name, an "ND" boolean. The detection limit value from Appendix X and a flagging code of "R." If the compound is detected but at less than the detection limit, the data shall be entered into the IRDMS in the same manner as a non-detect. However, the calculated value shall be recorded in the lot data package.



10.8 DATA REVIEW AND VALIDATION

An integral part of any QA Program is the review of data and its subsequent validation. The primary responsibility for this review and validation rests with the laboratory performing the analyses. Each data package must be reviewed with the data being validated prior to its submission to the Data Management System. Checklists, such as the examples in Appendix T, will be used to demonstrate that the data review was accomplished.

The data review and validation at the laboratory should include, but not be limited to, the following subjects:

- Completeness of laboratory data.
- Evaluation of data with respect to reporting limits.
- Evaluation of data with respect to control limits.
- Review of holding time data.
- Correlation of laboratory data from related laboratory tests.

The specific item for data review are covered in the Data Review Checklist, Appendix T.

Specific items for validation shall include, but are not limited to, the following:

- Examination of chain-of-custody records to ensure that custody was properly maintained.
- Comparison of data on instrument print-outs with data recorded on worksheets or in notebooks.
- Checking to ensure that the same calibration was used for all samples within a lot.
- Examination of chromatographic outputs and documentation of the reasons for manual integrations.
- Comparison of standard and sample preparation and injection records with instrument output to ensure that each output is associated with the correct sample.
- Examination of calibration and tuning results, to ensure that requirements are met.

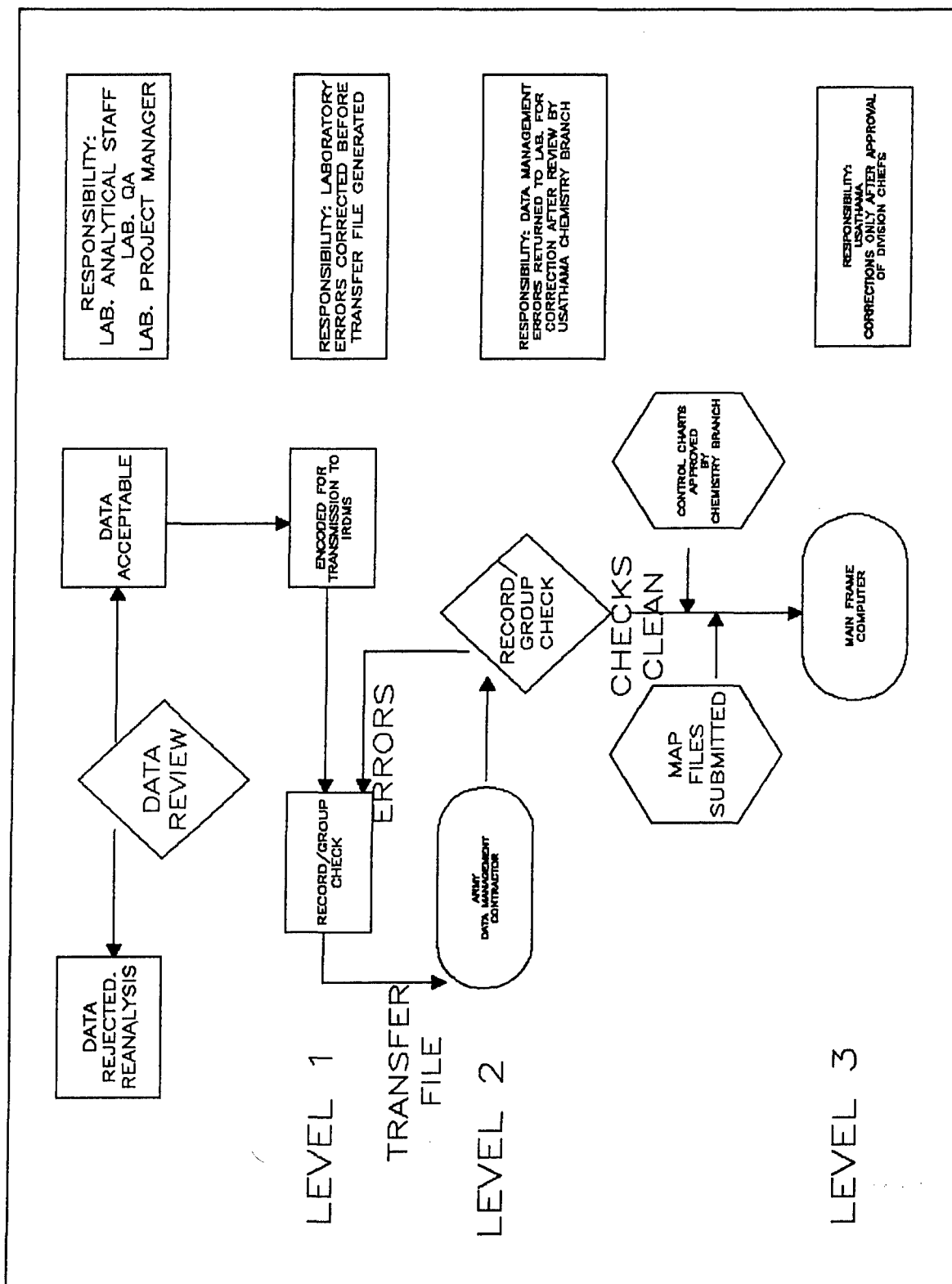


- Checking calculations on selected samples to ensure correctness.
- Checking that GC/MS library searches have been performed for all unknowns, as required, and that the results have been evaluated and recorded.
- Examination of all papers and notebooks to ensure that all pages are initialed, dated, and have sufficient explanation for the changes, and that all items are legible.
- Comparison of transfer file, record and group check results with analysis results.

Similar reviews are performed at USATHAMA once the data packages are received.



Figure 10-1.



11.0 INTERNAL QUALITY CONTROL CHECKS

11.1 INTRODUCTION

In addition to the requirements discussed thus far, QC samples must be analyzed to provide quantitative evidence that the entire method is performing comparable to or improved over the level demonstrated during certification. To comply with the USATHAMA QA Program, it is essential that controls are initiated during and maintained throughout the analysis of samples. Data generated from the control samples are plotted on control charts, which are used to monitor day-to-day variations in routine analyses.

The discussion of QC samples begins with guidance on the required analyses per lot (Section 9.4). The decision on how many QC samples are appropriate for each lot was based on analytical efficiency and the ability of the analyst to process the QC sample data and make decisions concerning problems on a daily basis. The approach described in the succeeding sections is the minimum acceptable performance for USATHAMA projects. This approach is intended to augment, not replace, existing laboratory QC practices. Problems detected by existing laboratory QC activities must not be ignored merely because the practices are not explicitly discussed in this document.

For multi-analyte methods, the selection of control analytes will be specified at the time the method is certified. As a rule, no less than 50 percent of the target analytes will be selected as control analytes, with the minimum number selected being 4. That is, for any method having four or fewer target analytes, all analytes will be selected as control analytes; for a method having 5 to 8 target analytes, 4 will be selected as control analytes; for each additional 1 or 2 target analytes, 1 additional control analyte will be selected. This means that a method having 9 or 10 target analytes will have 5 selected as control analytes while a method having 11 or 12 target analytes will have 6 control analytes and so forth. Exceptions will be specified in the appropriate standard method.

It should be noted, that although the specified levels of the control spikes are at 2XCRL and 10XCRL, consideration has to be taken as to the specific recoveries of the analytes to ensure that the chosen level falls within the certified range. That is, if greater than 100 percent recovery may be expected, then choosing a spike at the upper reporting limit could result in values above the certified range of the method. In that case, a spike level of 8XCRL would be more appropriate. The actual spiking levels will be recommended by USATHAMA Chemistry Branch at the time the method is certified.



11.2 CONTROL SAMPLES

Control samples are those samples that are introduced into the train of environmental samples to function as monitors on the performance of the analytical method. All required QC samples shall be prepared from standard matrices (Sections 5.6.1 and 5.6.2) or actual field samples (Class 1A) and processed through the complete certified analytical method. Stock solutions used to spike QC samples shall be prepared independently of stocks used for calibration standards or certification samples.

Numbers and concentrations of QC samples required for different certification classes, per lot of field samples, are summarized in Table 11-1.

11.2.1 TYPES OF CONTROL SAMPLES

The following types of QC samples shall be included in each analytical lot:

Class 1 and Class 1B Certified Method:

- Method Blank, to verify that the laboratory is not a source of sample contamination; and
- Spikes of all control analytes (required analytes spiked into QC samples) in standard matrices, to verify performance.

Class 1A Certified Method (GC/MS Only):

- Method Blank/Spike, to verify that the laboratory is not a source of sample contamination (non-surrogates) and to verify performance (surrogates); and
- Spikes of all control analytes (surrogate only) in every field sample, to observe recovery effects in the environmental matrix.

Class 2 Certified Method:

- Method Blank, to verify that the laboratory is not a source of sample contamination; and
- Spikes of all control analytes in standard matrices, to verify performance at the level demonstrated during certification and to distinguish between the response obtained from the blank.



Table 11-1. NUMBERS AND CONCENTRATIONS OF QC SAMPLES PER LOT

CLASS 1

- 1 - Standard Matrix Method Blank
- 3 - Standard Matrix Spikes
2, 10, & 10 CRL (approx)
- 1 - Standard Matrix Spike - Extended Range
100 CRL (approx) or Near Method Maxima

CLASS 1A

- 1 - Standard Matrix Method Blank/Spike
- 0 CRL Non-surrogate/10 CRL (approx.) Surrogate
- ALL - Natural Matrix (Field Sample) Spikes
10 CRL (approx.) Surrogate

CLASS 1B

- 1 - Standard Matrix Method Blank
- 1 - Standard Matrix Spike
10 CRL (approx.)

CLASS 2

- 1 - Standard Matrix Method Blank
- 1 - Standard Matrix Spike
1 CRL
- 1 - Standard Matrix Spike - Extended Range
100 CRL (approx.) or Near Method Maxima

Samples such as field blanks, trip blanks, rinse blanks, and field duplicates are sometimes collected by individuals performing sampling or contamination assessment. If so, they must be specified when planning field activities and explicitly described in the Project Workplan. These samples, when required, shall each be included at a rate of 1 per lot or 1 per 20 samples whichever is greater. Such field samples are not part of laboratory QC and will be treated by the laboratory simply as environmental samples. Evaluation of data from these field samples must be performed by the sampling or the significance of these results discussed. For metals analysis, the method of standard additions shall be required at the rate of 1 per 20 samples or



1 per lot, whichever is greater. A single concentration of each metal at near the middle of the concentration range of the method shall be used as the standard addition spike.

11.2.2 PREPARATION OF CONTROL SAMPLES

Because QC samples are used for rapid, daily control of the analytical process, most QC samples must be identifiable by the analyst. Sample numbers for QC samples must be assigned during the logging-in process. However, actual preparation of the QC samples shall be performed by the person who conducts the first step of the analytical method. This person is responsible for obtaining the correct volume/weight and type of standard matrix (Sections 5.6.1 and 5.6.2) or field sample (Class 1A) and for spiking the matrix with the required analytes at the correct concentration (Section 11.2.3).

The spiking solvents and procedures will be specified in the certified method. In general, however, the correct volume or weight of standard matrix/field sample for each method will be spiked with all control analytes using a minimum of spiking solution to prevent altering of the character of the matrix. Spiked samples, excluding water samples and VOA in soil, must be allowed to stand for one hour before continuing the analysis.

Validation of spiking solutions must be performed on a regular basis before the solution is used and not after as part of a correction action. The procedure to be followed is described in Appendix N.

11.2.3 CONCENTRATION AND FREQUENCY OF CONTROL SAMPLES

Method blanks contain no known additions of target analytes. 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 standard matrix QC blank and spike. Matrix spike and matrix spike duplicates may be required if specified in the contract task order. The following spiked QC samples shall be included in each analytical lot:

Class 1 Certified Method:

In addition to the method blank, independently prepared spiked standard matrix QC samples shall be included in each lot. Two spiked standard matrix QC samples shall contain all control analytes at a concentration near the upper limit of the certified range or approximately 10 CRL (not to exceed the upper limit of the certified range). The spiked concentration must be the same for both samples and should be commensurate with the allowed number of reportable significant figures. The third spiked standard matrix QC sample shall be prepared at the regulatory action level or approximately 2 CRL, as specified in the project contract.



Control analytes (required analytes spiked into QC samples) shall be specified in the USATHAMA standardized method. For multi-analyte methods, USATHAMA shall designate the required control analytes. The control analytes will be selected upon approval of certification. However, control limits will be initialized for all analytes. Those selected analytes will be used to demonstrate control of that method when analysis of all certified analytes is requested. The selection of control analytes will follow the guidelines of the QA Program, i.e., 50 percent of target analytes with a minimum of four selected.

For any subset of the certified analytes the QA guidelines will be maintained. If the original control analytes are not included in the subset target analytes, those original control analytes will be replaced on a one-to-one basis with analytes in the target subset. Selection of subset control analytes will need the approval of the Chemistry Branch Project Officer.

Any variations to the above will need the approval of the Chemistry Branch Project Officer prior to its implementation.

Control charts shall be maintained for each control analyte. The minimum number of required in-control data values, per lot, for establishing method control for multi-analyte methods are addressed in Section 11.5.2. and Table 11-2.

All samples in the same analytical lot need not be from the same installation. Analytical lots containing data from multiple installations must be entered into the USATHAMA IRDMS on a per-installation basis. Data from different installations shall be combined in the control charts (Section 11.4) to provide information about laboratory performance on all USATHAMA projects. Data from spiked QC samples shall be used to maintain control charts that pertain to all USATHAMA analyses.

Class 1A Certified Method (GC/MS only):

Independently prepared spiked standard and natural matrix samples shall be included in each lot. A single standard matrix QC sample, a method blank/spike, shall contain all certified surrogate analytes spiked at approximately 10 times the CRL (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. Spiked natural matrix QC samples shall consist of every field sample spiked with all certified surrogate analytes at approximately 10 CRL. The spike concentration must be the same for all samples. Two reportable significant figures shall be allowed for control sample results.

Control analytes shall consist of all surrogates specified in the USATHAMA standardized method. Additional non-surrogate target analytes may be specified by the USATHAMA Project Officer for spiking (standard matrix only). Control charts shall be maintained for only surrogate control analytes spiked in standard matrix samples. The minimum number of required in-control data values, per lot, for establishing method control for multi-analyte methods are addressed in Section 11.5.2. and Table 11-2.



The results of natural matrix surrogate spikes are reported to the IRDMS. In addition, the recoveries of the natural matrix surrogate spikes must be taken into account in the evaluation of matrix effects of specific samples. When the recovery of the natural matrix surrogate spike(s) is markedly different from historical data, then the associated sample is entered into the IRDMS with a flagging code of Q, to show that there were problems with its surrogate recovery. In order to aid in the evaluation of natural matrix surrogate recovery, the data from the natural matrix surrogate spike recovery will be maintained on forms as described in Appendix V. A single form will be used for each surrogate in each lot and will become part of the data package for that lot.

Alternatively, if a laboratory-wide computerized data management system is available, data or surrogates may be generated electronically and output on forms or control charts derived for that purpose. In either case, documentation must be available to track the matrix effect of the samples using the surrogates. The data from the natural matrix surrogate spike recovery will be maintained and plotted on charts similar in format to control charts. The chart will be prepared using the first 20 recoveries generated from the determination of the natural matrix surrogate spikes during in-control analyses, with the proviso that the recoveries used do not exhibit matrix effects. The mean of the chart will be the mean of the recoveries of the surrogate in these first 20 analyses. The upper and lower limits will be set at plus or minus 3 standard deviations from that mean. Software to accomplish this will not be provided by USATHAMA.

Class 1B Certified Method:

In addition to the method blank, an independently prepared spiked standard matrix QC sample shall be included in each lot. The spiked standard matrix QC sample shall contain all control analytes at a concentration near the upper limit of the certified range or approximately 10 CRL (not to exceed the upper limit of the certified range) and should be commensurate with the allowed number of reportable significant figures.

Control analytes (required analytes spiked into QC samples) shall be specified in the USATHAMA standardized method. For multi-analyte methods, USATHAMA shall designate the required control analytes. Control charts shall be maintained for each control analyte. The minimum number of required in-control data values, per lot, for establishing method control for multi-analyte methods are addressed in Section 11.5.2.

All samples in the same analytical lot need not be from the same installation. Analytical lots containing data from multiple installations must be entered into the USATHAMA IRDMS on a per-installation basis. Data from different installations shall be combined in the control charts (Section 11.4) to provide information about laboratory performance on all USATHAMA projects. Data from spiked QC samples shall be used to maintain control charts that pertain to all USATHAMA analyses.

Class 2 Certified Method:

In addition to the method blank, each lot must include one spiked QC sample. The concentration of the spiked sample shall be the CRL from certification which establishes the



level which can be distinguished from a blank. Control charts are not maintained for Class 2 analyses.

Extended Range Certifications:

For method certifications (Class 1, Class 1A, and Class 1B) involving concentration ranges that extend to levels greater than 20 times the CRL but less than 100 CRL, an additional standard matrix QC sample containing all control analytes spiked at a level near the upper limit of the certified range shall be required. For each additional order of magnitude certified, an additional standard matrix QC sample is required. Data generated from these additional QC samples shall be used to maintain control charts as specified for all USATHAMA analyses.





11.3 DATA REPORTING for QC

11.3.1 CLASS 1, CLASS 1A, and CLASS 1B CERTIFIED METHODS

The results for each analyte in the spiked QC sample shall be determined using the same acceptable calibration curve that is used for environmental samples in the lot. Raw values below the CRL will be reported as "less than" the reporting limit (Section 10.4.1). Results for QC samples shall not be corrected, except as described below. Because all spike levels must be within the certified range, no dilutions should be required. Data shall be reported in the USATHAMA IRDMS, as described in Section 10.6, using the correct number of significant figures (maximum of 3 for Class 1 and Class 1B, 2 for Class 1A and Class 2).

Each day of analysis, the analyst shall quantify each analyte in the method blank and spiked QC samples. A new lot of samples shall not be introduced into the analytical instrument until results for QC samples in the previous lot have been calculated, plotted on control charts as necessary, and the entire analytical method shown to be in control. If time is a constraint, the calculation of associated environmental sample results may be postponed until a later date. The analyst should maintain control charts by the instrument so that the results of QC samples could be hand-plotted, in order to have an early indication of problems.

Data from the method blank shall be reported, usually as "less than" the CRL for each analyte. Any values above the CRL shall be reported as determined. Corrections to the QC samples, necessitated by background levels in the method blank, shall be performed using instrument response values and not the found values calculated from the linear calibration curve. (Exceptions to this convention for specific methods will be specified in the appropriate analytical method). Method blank correction for non-linear calibrations requires contacting the USATHAMA Chemistry Branch for instructions on a case-by-case basis. Entries into the USATHAMA IRDMS shall be in terms of concentration. The importance attached to finding measurable concentrations in the method blank is dependent on analyte and method. In the Project QC Plan, each laboratory must describe its procedure for assessing method blank results and identifying laboratory contamination problems.

11.3.2 CLASS 2 CERTIFIED METHODS

Method blank, dilution, and accuracy corrections are not performed for Class 2 analyses. The results for samples analyzed by Class 2 certified methods are measured in relation to the CRL (two significant figures) and reported as "less than, equal to, or greater than" the CRL. A tested concentration range is not applicable since only the CRL concentration is tested.



11.4 CONTROL CHARTS

Control charts are not used with Class 2 certified methods. 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 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 shall not be adjusted for accuracy.

Although tabulations of the various statistical parameters can be used to evaluate if a datum falls within the prescribed limits, trends are very difficult to discern from tables. Therefore, control charts shall consist of tabulated data and graphical portrayals of the information described below. Software packages that can be used to construct charts will be provided by USATHAMA and the use of the USATHAMA supplied software is required.

In the initial construction of the control charts, data from the laboratory certification analyses will be used. Data from spiked QC samples within a lot will be compared to control chart limits to demonstrate that analyses of the lot are under control, and will be used to update the charts. $\bar{x}$ - R control charts will be used in this QA Program.

Each control chart shall include the following information:

- Analyte;
- Method number;
- Laboratory;
- Spike concentration;
- Matrix; and
- Chart title - select one of the following:
 - 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



- Three letter lot designation for each point, shown on the x-axis;
- Percent Recovery (for $\bar{x}$ control charts) or Range (for R control charts) along the y-axis;
- Upper control limit (UCL), on $\bar{x}$ and R control charts;
- Upper warning limit (UWL)*, on $\bar{x}$ and R control charts;
- Mean, on $\bar{x}$ and R control charts;
- Lower warning limit (LWL)*, on $\bar{x}$ control charts; and
- Lower control limit (LCL), on $\bar{x}$ control charts.

For some analytes specified by USATHAMA, warning limits on $\bar{x}$ charts will be deleted and replaced by modified control limits based on data quality specifications. See Appendix O for details.

11.4.1 SINGLE DAY $\bar{x}$ - R CONTROL CHARTS

Control charts are prepared for each control analyte using data from the duplicate spiked QC samples in each lot to determine percent recovery:

$$\frac{\text{*Found Concentration}}{\text{Spiked Concentration}} \times 100$$

(* Method Blank correction addressed in Section 11.3.1). Use of percent recovery allows for minor variations in spiking solution concentrations.

To prepare control charts, the analyst should have access to the following data:

- Percent recovery of each analyte in the two high concentration spiked QC samples (Class 1);
- Average ($\bar{x}$) percent recovery for the two spiked QC samples (Class 1) in each lot; and
- Difference (R) between the percent recoveries for the two spiked QC samples (Class 1) in each lot.

The initial control chart shall be prepared using the four days of certification data closest to the spiking concentration used during analyses. The average $\bar{x}$ ($\bar{x}$), average range (R), and control limits for $\bar{x}$ and R shall be updated after each in-control lot for the first 20 lots. Limits



established after lot 20 shall be used for the next 20 lots. Control charts shall be updated after each 20 lots, thereafter, using the most recent 40 points. In interpreting the control charts developed for the initial lots (lots 1-20), the limits established from the previous lots will be used to control the current lot. When modified limits (see Appendix O) are established, data for samples will be accepted if the control data falls between the modified limits. If modified limits have not been established, data for samples will be accepted based on 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 control limits. Out-of-control or outlier points should be plotted; however, such lots are not utilized in lot number requirements or control limit calculations.

The formulae used to establish and maintain control charts for duplicates are as follows:

$$\text{Average: } \bar{\bar{x}} = \frac{\sum \bar{x}}{K}$$

$$\text{Range: } \bar{R} = \frac{\sum R}{K}$$

where:

$\bar{\bar{x}}$ = between group average of the pairs (within group) average recovery;

$\bar{x}$ = average within group recovery for data pairs;

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

K = cumulative number of pairs in data base.

$$\text{UWL on Average: } UWL_{\bar{x}} = \bar{\bar{x}} + 1.25 \bar{R}$$

$$\text{UCL on Average: } UCL_{\bar{x}} = \bar{\bar{x}} + 1.88 \bar{R}$$

$$\text{LWL on Average: } LWL_{\bar{x}} = \bar{\bar{x}} - 1.25 \bar{R}$$

$$\text{LCL on Average: } LCL_{\bar{x}} = \bar{\bar{x}} - 1.88 \bar{R}$$

$$\text{UWL on Range: } UWL_R = 2.511 \bar{R}$$



UCL on Range: $UCL_R = 3.267 \bar{R}$

LWL on Range: $LWL_R = 0$

LCL on Range: $LCL_R = 0$

One possible format for maintaining $\bar{x}$ - R chart data in both tabulated and graphic form is shown in Figures 11-1 and 11-2. Examples of $\bar{x}$ - R data and charts are provided in Appendix L.

See Appendix O for discussion on Modified Limits

All recoveries shall be 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 shall be tested as an outlier using Dixon's Test at the 98 percent confidence level (Appendix K). If the datum is not classified as an outlier by the test, the point shall be included in updating the control chart limits. If the datum is classified as an outlier, it shall not be used in updating the control chart limits. Method control shall be judged according to the criteria in Section 11.5. Range data are not subject to outlier testing.

After the first 20 in-control sample lots, control limits shall be recalculated using only in-control data points. The control limits shall then be drawn backward to encompass all previous points. Any points falling outside the control limits (UCL or LCL) shall be dropped and the control limits recalculated using only points between the UCL and LCL. This practice of dropping points and recalculating limits is only performed once. Charts will then be updated with the newly calculated control limits and all points plotted. Lots associated with points outside the new control limits may require resampling and/or reanalysis as determined by the USATHAMA Project Officer on a case-by-case basis. These limits shall then be used to control analysis of the next 20 lots. Once 60 or more lots are analyzed by a particular method, control limits are recalculated based upon the 40 most recent in-control lots, i.e., control limits for the 60th lot are based on lots 21-60 (40-point slide).



Laboratory _____ Date _____

Method of Test or Operation _____

Reference Value _____ Increment of Measurement _____

[illegible]

Totals ΣX _____ ΣR

X_j = observed value R = largest - smallest

K = sets of values CL = control limit

Σ = summation WL = warning limit

U = upper L = lower

$$D_4 = 3.267 \text{ for } n = 2; 2.575 \text{ for } n = 3$$
$$A_2 = 1.880 \text{ for } n = 2; 1.023 \text{ for } n = 3$$
$$1. \quad R = \Sigma R \div K$$

$\frac{0}{0}$

$$2. \quad UCL_R = D_4 \times \bar{R}$$
$$\underline{\hspace{1cm}} = \underline{\hspace{1cm}} \times \underline{\hspace{1cm}}$$
$$3. \quad UWL_R = 2/3(D_4 \bar{R} - \bar{R}) + \bar{R}$$
$$= 2/3(\underline{\hspace{1cm}} - \underline{\hspace{1cm}}) + \underline{\hspace{1cm}}$$
$$4. \quad \bar{\bar{X}} = \Sigma \bar{X} \div K$$
$$\frac{1}{2} = \frac{1}{2} \div 1$$
$$5. \quad CL_{\bar{Y}} = A_2 \times \bar{R}$$
$$\underline{\quad} = \underline{\quad} \times \underline{\quad}$$
$$6. \quad WL_{\bar{Y}} = 2/3 \times CL_{\bar{Y}}$$
$$= \frac{2}{3} x$$
$$7. \quad UCL_{\bar{Y}} = \bar{\bar{X}} + CL_{\bar{Y}}$$
$$= +$$
$$8. \quad UWL_Y = \bar{X} + WL_Y$$
$$= +$$

9. $LWL_{\bar{Y}} = \bar{X} - WL_{\bar{Y}}$

$$10. \quad LCL_{\bar{X}} = \bar{\bar{X}} - CL_{\bar{X}}$$

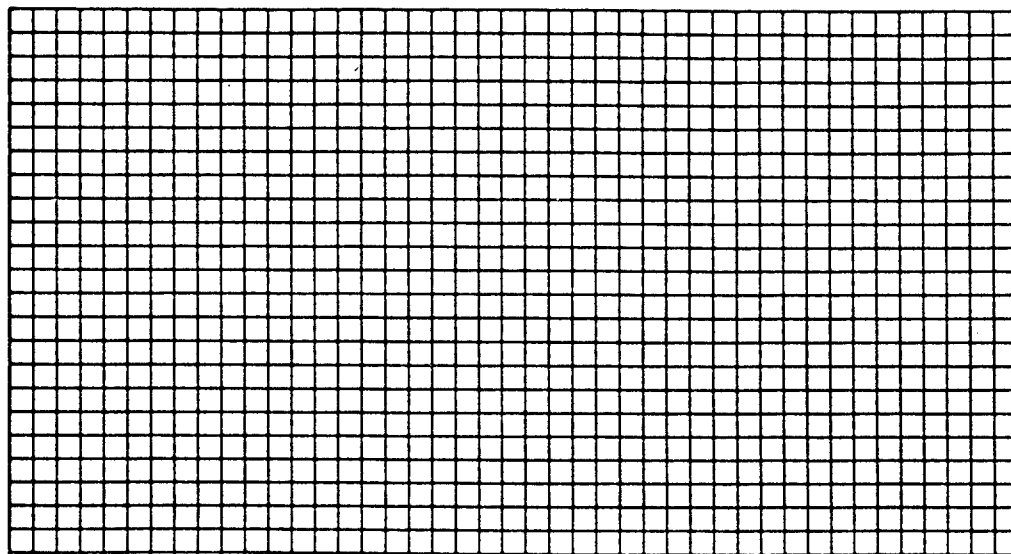
11



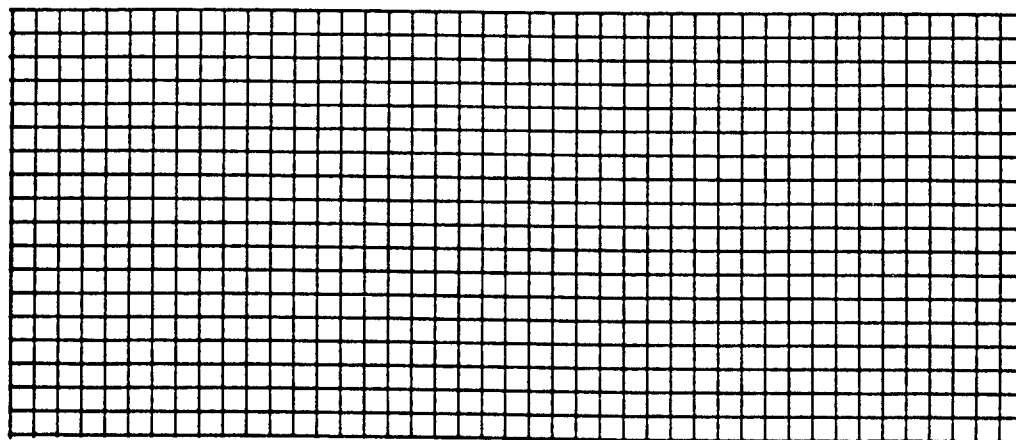
Figure 11-2. Sample $\bar{x}$ - R CONTROL CHART PLOTTING FORMATLaboratory Quality Control Worksheet -- $\bar{x}$ - R Chart

Operation _____ Date _____

Averages



Ranges



Sample Number

Directions:

1. Draw $\bar{R}$ line _____
2. Draw UCL_R line _____
3. Draw UWL_R line _____
4. Plot R 's as generated
5. Draw $\bar{X}$ line _____
6. Draw $UCL_{\bar{X}}$ line _____
7. Draw $UWL_{\bar{X}}$ line _____
8. Draw $LWL_{\bar{X}}$ line _____
9. Draw $LCL_{\bar{X}}$ line _____
10. Plot $\bar{X}$'s as generated



If the method is judged to be out-of-control (Section 11.5) and reanalysis occurs, no point from the initial analysis may be used to update charts.

11.4.2 THREE-POINT MOVING AVERAGE CONTROL CHARTS

Moving average control charts shall be maintained for each control analyte spiked in the single low concentration spiked QC sample (Class 1), single high concentration spiked QC sample (Class 1B), surrogate spiked standard matrix sample (Class 1A), or the additional spiked QC sample(s) for extended ranges (Section 11.2.3). The X - R three-point moving average control chart shall be constructed for each control analyte as follows:

- Use percent recovery to allow for minor variations in spiking concentration;
- 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, UWL, UCL, LWL, and LCL for the control charts are calculated using the following formulae:

$$\text{Average: } \bar{\bar{x}} = \frac{\sum \bar{x}}{K}$$

$$\text{Range: } \bar{R} = \frac{\sum R}{K}$$

where:

$\bar{\bar{x}}$ = between group average of the three points (within group) average recovery;

$\bar{x}$ = average within group recovery for the three points;

R = within group difference between recoveries for data sets; and



$\bar{R}$ = between group average of the three points (within group) average range

K = cumulative number of sets in data base.

UWL on Average*: $UWL_{\bar{x}} = \bar{\bar{x}} + 0.682 \bar{R}$

UCL on Average: $UCL_{\bar{x}} = \bar{\bar{x}} + 1.023 \bar{R}$

LWL on Average*: $LWL_{\bar{x}} = \bar{\bar{x}} - 0.682 \bar{R}$

LCL on Average: $LCL_{\bar{x}} = \bar{\bar{x}} - 1.023 \bar{R}$

UWL on Range: $UWL_R = 2.050 \bar{R}$

UCL on Range: $UCL_R = 2.575 \bar{R}$

LWL on Range: $LWL_R = 0$

LCL on Range: $LCL_R = 0$

All data shall be 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 shall be tested as an outlier using Dixon's Test at the 98 percent confidence level (Appendix K). If the datum is not classified as an outlier by the test, the point shall be included in updating the control chart limits. If one of the individual measurements is an outlier, it shall be used in calculating the three-point moving average for plotting only, but is then excluded from calculations which are based on the three most recent acceptable individual points and the control chart limits determined accordingly. Method control shall be judged according to the criteria in Section 11.5. Range data are not subject to outlier testing.

After the first 20 in-control sample lots, control limits shall be recalculated using only in-control data points. The control limits shall then be drawn backward to encompass all previous points. Any points falling outside the control limits (UCL or LCL) shall be dropped from the calculations (but left on the charts) and the control limits recalculated using only points between the UCL and LCL. This practice of dropping points and recalculating limits is only performed once. Charts will then be updated with the newly calculated control limits and all points plotted. Lots associated with points outside the new control limits may require resampling and/or

See Appendix O for discussion on Modified Limits.



reanalysis as determined by the USATHAMA Project Officer on a case-by-case basis. These limits shall then be used to control analysis of the next 20 lots. A maximum of the 40 most recent lots will be used to recalculate control limits for 60 or more lots (40-point slide).

An example of data tabulation and plotting using moving average $\bar{x}$ - R charts is shown in Appendix M.

11.5 OUT-OF-CONTROL SITUATIONS

Failure to meet calibration criteria, record keeping omissions, improper sampling technique, and improper storage or preservation of samples are all conditions that affect data quality and require investigation/correction. However, this section of the USATHAMA QA Program describes only evaluations performed by the analyst, in consultation with the QAC, to determine whether the entire analytical method is in control. These evaluations must be done daily so that action can be taken immediately to investigate and correct the problem. Failure to take immediate action may necessitate discarding large quantities of data and reacquiring, preparing, and reanalyzing samples processed after the problem was detected.

For both duplicate spiked QC results (Section 11.4.1) and moving averages (Section 11.4.2), a single mean ($\bar{X}$) outside of modified limits requires immediate investigation/corrective action. When two or more successive lot means for duplicate spiked QC data are outside normal control limits but within modified limits, investigation/corrective action should be taken even though the data from these lots are acceptable. For moving averages, a single mean outside of normal control limits but within modified limits requires investigation/corrective action even though the data are acceptable.

11.5.1 HOLDING TIMES

Any sample or sample extract held beyond the time periods specified in Appendix H shall be deemed out-of-control. These samples should not be analyzed unless a written, incident-specific exception is received from the USATHAMA Chemistry Branch. Sampling and laboratory schedules, and budgets, should be coordinated to avoid holding time violations.

11.5.2 $\bar{x}$ Control Charts

An out-of-control situation for $\bar{x}$ control charts may be indicated by:

- 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 central line;
- 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.

Whenever one of these conditions is detected, the analyst and QAC must investigate to determine the cause and document actions taken. Data acquired concurrently with one of these conditions shall be discarded and samples reanalyzed unless the investigation of the problem proves that the analysis was in control, or modified control limits are being used to determine acceptability of data (See Appendix O). Justification for the acceptance of data must be provided with the weekly quality control submission.

The analyst will determine whether all sample analyses by a multi-analyte method should cease, in the following way:

- Plot average percent recovery ($\bar{x}$) for each analyte.
- If the points for at least two thirds (see Table 11-2) of the control analytes for a multi-analyte method are classified as in-control, based on the conditions described above, the method is in control and environmental sample data may be reported (providing that the condition of two consecutive out-of-control points has not occurred). The conditions which may have caused more than one third of the control analytes to fail the control criteria shall be investigated and corrected as necessary. All activities shall be documented. The data points indicating possible error shall be annotated with a reference to the investigation and to the fact that the method met control criteria.
- 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 out-of-control. Analyses must cease, the cause must be investigated and corrected, and a determination made by the USATHAMA Chemistry Branch of whether the lot must be reanalyzed.
- If data points for fewer than 2/3 of the control analytes are classified as in control (more than 1/3 meet one of the out-of-control conditions), the method is considered to be out-of-control and all work on that method (including sample preparation) must cease



immediately. No data for environmental samples in that lot may be reported. Efforts must be initiated to determine the cause of the problem. If the problem is instrumental or specific only to preparation of that lot, samples prepared after the out-of-control situation occurred may be processed after the instrumental system is repaired and recalibrated, provided holding times are not exceeded. If no specific cause can be assigned, the instrument should be recalibrated and all samples prepared subsequent to the last in-control lot should be prepared. In any case, the out-of-control lot must be reanalyzed. The out-of-control situation and corrective actions taken must be fully documented. Each point shall be annotated with a reference to the investigation and to the disposition of samples and results.

- The establishment of overall method control for analyses may not be accurate for describing a particular analyte(s). For analyses where control cannot be established for certain control analytes (i.e., loss of surrogate due to volatility), such analyte results may still be deemed as out-of-control even though the method is considered in control. The evaluation of control in such instances will be handled on a case-by-case basis.

If a lot is still out of control after reanalysis, all method-related activities shall stop immediately. A detailed laboratory-wide investigation shall be conducted to isolate and correct faulty operations. Sample security, integrity of standards, reagents, glassware, laboratory notebooks, instrument performance, and adherence to certified methods should be included in the investigation and the findings/corrective actions documented.

11.5.3 R CONTROL CHARTS

An out-of-control situation for R control charts may be indicated by:

- A value above the UCL;



Table 11-2. MINIMUM NUMBER OF IN-CONTROL POINTS
FOR MULTI-ANALYTE METHODS

<u>Required Control Analytes Per Method</u>	<u>Required Number of Data Values Falling Between the UCL and LCL</u>
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



- A series of five consecutive points going in an upward direction;
- A cyclical pattern of control values; or
- Two consecutive points between the UWL and UCL.

Whenever one of the conditions is detected, the analyst and QAC must investigate. Criteria for determining if a method is in control are the same as those described in Section 11.5.2. Out-of-control on range charts bears as much weight as out-of-control on accuracy charts.



12.0 PERFORMANCE AND SYSTEM AUDITS

An audit is a systematic evaluation to determine the quality of operation of some system or function. As applied in the USATHAMA QA Program, an audit may be external or internal.

12.1 EXTERNAL

External audits are conducted by representatives of the USATHAMA Chemistry Branch or their representatives. After reviewing the proposed Project QC Plan, the Contractor Laboratory may be visited to discuss any weaknesses in the plan, to evaluate the laboratory's capability to implement the plan, and to discuss any discrepancies in the certification documents, etc. During this visit, the USATHAMA representative will fill out the Audit Checklist (Appendix U). Copies of the completed checklist will be provided to the USATHAMA Project Officer, the Contractor Project Manager, the Contractor Analytical Task Manager, the Contractor QAC, and the USATHAMA Chemistry Branch. If deficiencies are of a serious nature, copies may be forwarded to the Contracting Officer at Procurement for official documentation and action. The visit may occur before analyses of field samples are initiated by the laboratory.

After initiation of the analyses by the Contractor Laboratory, a USATHAMA representative may visit the field activities or the laboratory to evaluate the effective implementation of the Project QC Plan. Any project related activities may be evaluated during the visit (Appendix U). Any documents or data required by the QA Program are eligible for inspection. Any aspect of the internal audit may be monitored. Findings will be reported to the USATHAMA Project Officer, the Contractor Project Manager, the Contractor Analytical Task Manager, the Contractor QAC, and the USATHAMA Chemistry Branch. If deficiencies are of a serious nature, copies may be forwarded to the Contracting Officer at Procurement for official documentation and action.

Scheduling/completion of the visits noted above does not preclude additional visits, as deemed necessary or desirable.

12.2 INTERNAL

Audits of critical functions by the project QC staff (QAC or representative of the QAC) will include:

- Verification that standards, procedures, records, charts, magnetic tapes, etc., are properly maintained;



- Verification that actual practice agrees with written instructions; accomplished through the use of a systems audit where a selected method is monitored through all the steps of its performance. This system audit must be accomplished at least once each quarter, if the laboratory effort is long term; or once a month if the laboratory effort is short term. Methods must be selected so that all phases of a laboratory's effort is monitored, to include but not be limited to sample logging, chain of custody, sample preparation, standard preparation, extract storage and analysis and data reduction;
- Verification that QA records are adequately filed and maintained so as to assure protection and retrievability; and
- Assessment of results of QC sample analyses.

Auditing will consist of observations and notations as to whether approved practices are followed. A formal audit report comprised of summary findings shall be distributed to the Project Manager, Analytical Task Leader, and USATHAMA. Deviations will be noted and discussed with the staff member, appropriate management, and with USATHAMA. The audit and findings, both compliance and non-compliance, must be documented in a bound logbook, or permanently attached and maintained as part of the QA documentation. The QA office will maintain by project, a file(s) of audit reports and findings, copies of reports and findings that cover more than one project shall be maintained in each project file. At the conclusion of a project or task order, copies of the QA file shall be transmitted to the USATHAMA Chemistry Branch, along with the data packages.



13.0 INSTRUMENT MAINTENANCE

This section establishes procedures for maintaining test and measurement equipment used to conduct analyses, in such areas as instrument maintenance, service contracts, and absolute physical or electronic calibration. Chemical calibration is discussed in Section 8.

The calibration policies and procedures set forth will apply to all test and measuring equipment. All test and measuring instruments fall into two general categories: those which are calibrated prior to each use and those which are calibrated on a scheduled, periodic basis.

All equipment to be calibrated will have an assigned record number permanently affixed to the instrument. A label will be affixed to each instrument showing: description, manufacturer, model number, serial number, date of last calibration or maintenance, by whom calibrated/maintained, and due date of next servicing. Calibration reports and compensation or correction figures will be maintained with the instrument. Thermometers are exempt from the labeling requirement, but not from the calibration requirement.

A written stepwise calibration procedure must be available for each piece of test and measurement equipment. Any instrument which is not calibrated to within the manufacturer's original specifications must display a red warning tag to alert the analyst that the device carries only a "limited calibration." Equipment unable to meet approved calibration specifications shall not be used for sample analysis.

It is the contractor's responsibility to maintain an adequate supply of critical spare parts to minimize instrument down-times.

13.1 CALIBRATION IDENTIFICATION

Instruments past due for calibration or maintenance must be immediately removed from service, either physically or, if this is impractical, by tagging, sealing, labeling, or other means.

The labeling and recording system extends to calibration or maintenance services provided to the Contractor Laboratory by other organizations. Certifications and reports furnished by them should be filed and made a part of the required record keeping system.

Equipment in "Calibrate Before Use" (CBU) status must be administratively sequestered to avoid accidental use without calibration.



13.2 CALIBRATION STANDARDS

All physical or electronic measurements or calibrations (excluding chemical calibration curves) performed by or for the Contractor Laboratory must be traceable, directly or indirectly, through an unbroken chain of properly conducted calibrations (supported by reports or data sheets) to the NIST. Reports must be up-to-date for each reference standard and each subordinate standard used for calibration of test and measurement equipment. When calibration services are performed by a non-contractor laboratory organization, copies of reports, and records showing traceability to the NIST should be immediately available. These records may be inspected during laboratory audits.

13.3 CALIBRATION FREQUENCY SCHEDULE

At a minimum, calibration and maintenance intervals for complex or sensitive laboratory instruments must be those recommended by the respective manufacturers, unless experience dictates a shorter interval. When the manufacturer has not specified a calibration interval for his equipment, the interval will be established in writing by the calibration group servicing the laboratory. Adherence to the schedule is mandatory. The fact that these checks may be scheduled and performed by an outside source does not exempt the laboratory from its responsibility for identifying, monitoring and controlling calibration intervals, and ensuring that checks are made on time.

13.4 EXAMPLES

Routine, "absolute" calibration is not the same as chemical calibration, where the relationship between instrument response and concentration is established. "Absolute" calibration ensures that the perceived instrument response corresponds to the correct physical signal that should produce that response. Examples of equipment that must be "absolutely" calibrated include, but may not be limited to, the following:

- Balances -- These are the clearest examples of equipment requiring calibration. NIST-certified weights are used to ensure the accuracy of measurements.
- Thermometers -- NIST-certified thermometers are used to verify the accuracy of measurements.



- Other Temperature Sensors and Controllers -- For analytical equipment that incorporates temperature sensing or control, the accuracy of the sensors and controllers will affect method performance. When a method

specifies an injector temperature of 100°C, the analyst must be sure that the instrument settings for 100°C actually corresponds to that temperature. Oven temperatures (e.g., drying ovens, GC ovens) must be accurately known. Equipment manufacturers describe procedures for temperature calibration, using either NIST-calibrated thermometers or measured electrical signals.

- Flow Controllers -- Measuring and controlling gas and liquid flow are integral parts of many instrumental analysis systems. The devices used to measure/control must be calibrated to ensure that actual flow corresponds to instrument readings or settings. ICAP, IC, GC, GC/MS, and HPLC are examples of systems that must be calibrated for flow.
- Autoinjectors -- The actual volume injected into the analytical system must correspond to the instrumental settings for the intended volume. This calibration is particularly critical when absolute analyte response (e.g., peak height) is used for quantification (as opposed to the ratio of analyte peak height to internal standard peak height).
- Recorders -- When physical records (e.g., strip charts) are used for quantification, the recorder response must correspond to the electronic signal received. If the basis of quantification is a linear relationship between response and concentration, the recorder must exhibit linear response to linear changes in electric signals.





14.0 SPECIFIC ROUTINE PROCEDURES USED TO ASSESS DATA PRECISION, ACCURACY AND COMPLETENESS

14.1 STATISTICAL ANALYSIS OF CLASS 1, CLASS 1A, AND CLASS 1B PRECERTIFICATION PERFORMANCE DATA

Data obtained during precertification calibration analyses shall be tested for linearity using Lack of Fit (LOF) and Zero Intercept (ZI) tests (Appendix B). These statistical tests are performed by the USATHAMA software. Non-linear or non-Zero Intercept calibration curves may be acceptable but must be discussed with USATHAMA prior to use.

14.2 STATISTICAL ANALYSIS OF CLASS 1, CLASS 1A, AND CLASS 1B CERTIFICATION PERFORMANCE DATA

This section describes the statistical analysis of data obtained during certification analyses. The calculations described in the following sections are contained in computer software developed by USATHAMA.

The statistical calculations compare the found concentration of the standard spiked samples with the known target spiked concentration. The found concentrations must have been determined from calibration curves constructed according to the standardized method. Recovery factors shall not be used to correct found concentrations used during analysis of certification data. The calculations must be performed for each target analyte in a method. The reported found concentrations and statistical analysis values obtained during Class 1, Class 1A, and Class 1B certification activities should use at most three significant figures.

14.2.1 LACK OF FIT (LOF) AND ZERO INTERCEPT (ZI) TESTS

All data must have been collected during periods when instrumental calibration was in control (within +/- 10 percent of the mean response for inorganics analyses in surface/groundwaters and within +/- 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 found concentrations are compared to the target concentrations. This relationship must be tested because calculation of the CRL assumes a linear relationship.

Data obtained during certification analyses shall be first examined for any outliers (Appendix Y) before being tested for linearity using the LOF and ZI tests (Appendix B). In the absence or replacement of an outlier, data from each of the 4 days (Class 1 and Class 1B) or single day (Class 1A) of certification analyses shall be pooled and tested for LOF. All LOF test



calculations and results shall be included in the Performance Data Package. If the pooled data fails the LOF test at the 95 percent confidence level, the USATHAMA Chemistry Branch must be contacted for discussion and guidance.

14.2.2 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 which may be reported. This concentration is the CRL. For USATHAMA projects, CRLs shall be determined by using the USATHAMA program with 95 percent confidence limits. This CRL is associated with the entire method and reflects all sample preparation and measurement steps. Contractors are cautioned about two items. First, this approach differs from instrumental detection limit (e.g., three times the blank signal to noise ratio); the method CRL will likely be considerably higher than the instrumental detection limit. Second, because the CRL reflects use of the entire method, all steps of all analyses must always be performed in exactly the same way.

The CRL is derived from the following assumptions:

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

Based on these assumptions, the least squares linear regression line of the form;

$$(1) \quad Y = Y_0 + bX$$

is determined, where:

Y = Found concentration;

Y_0 = Y axis (found concentration) intercept;

b = Slope of the line; and

X = Target concentration.

The certification performance data (X , Y paired data) are used to determine the least squares regression line according to the following formula, which assume that errors occur only in the found concentration:



$$(2) \quad \text{Slope} = b = \frac{N \sum X_i Y_i - \sum X_i \sum Y_i}{N \sum X_i^2 - (\sum X_i)^2}$$

where:

N = Number of data points;

X_i = The i -th target concentration; and

Y_i = The i -th found concentration.

$$(3) \quad Y \text{ Axis Intercept} = Y_0 = \frac{\sum Y_i - b \sum X_i}{N}$$

where:

b = Slope of the least squares linear regression line, from Equation 2.

The upper confidence limit about the regression line is given by:

$$(4) \quad Y = Y_0 + bX + S_{Y.X} t \left[1 + \frac{1}{N} + \frac{(X_i - \bar{X})^2}{\sum (X_i - \bar{X})^2} \right]^{1/2}$$

The lower confidence limit about the regression line is given by:

$$(5) \quad Y = Y_0 + bX - S_{Y.X} t \left[1 + \frac{1}{N} + \frac{(X_i - \bar{X})^2}{\sum (X_i - \bar{X})^2} \right]^{1/2}$$

where:

$$S_{Y.X} = \left[\frac{\sum \{Y_i - (\bar{Y} + b(X_i - \bar{X}))\}^2}{N - 2} \right]^{1/2}$$

Y_0 = Calculated Y axis intercept;

t = Student's t for 2-tailed $P = 0.10$ and $N-2$ degrees of freedom;



$\bar{x}$ = The average of all target concentrations; and

$\bar{y}$ = 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 USATHAMA computer software is shown in Appendix C.

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 shall not be less than the lowest tested concentration. The CRL for Class 1 and Class 1B is reported to three significant figures. However, the CRL for Class 1A may only be reported to two significant figures.

The calculations described above must be performed on the entire certification performance data set in order to determine the method accuracy, as described in Section 14.2.3. If the calculated reporting limit for the complete data set (Class 1 and Class 1B only) is higher than required, points may be sequentially truncated, starting with the highest concentration. Truncation is not allowed for Class 1A certification unless certification is performed over an extended range and therefore result in the analysis of more than three positive standards. At no time will truncation be allowed that results in a line using less than three standards. The calculations described above shall be performed using the truncated data set to obtain a new calculated reporting limit. This procedure may be repeated, sequentially dropping the next highest concentration, until a satisfactory calculated reporting limit is obtained. The following limitations shall apply to the Class 1 and Class 1B truncation procedure:

- The data set must include the blank and the three lowest concentrations (0.5 TRL, 1 TRL, and 2 TRL); and
- After each truncation, the slope of the least square linear regression line shall not change by more than 10 percent from the slope for the total data set. If the slope changes by more than 10 percent after dropping a concentration, the calculated reporting limit may not be used as the CRL and further truncation is not acceptable.

The data 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.



The results for the total data set and each truncated set shall be provided in the Certification Performance Data Package.

These calculations are performed by the USATHAMA computer software. The CRL calculations cannot be performed for Class 2 methods. The TRL becomes the CRL for Class 2, which is only reported to two significant figures.

The criterion of detection (COD) can be calculated from the same data set as the CRL. The COD is a value below the CRL but above the instrument detection limit that takes into account the beta risk of 5 percent. The COD is the value of X corresponding to a point on the regression line where the value of Y equals the value of Y on the upper confidence limit curve at $X = 0$.

Data values above the CRL are reported as the found value. Data values below the CRL but above the COD are reported as the found value with a flagging code of "P." Data values below the COD are reported as LT CRL with a flagging code of "P."

14.2.3 ACCURACY

As calculated according to Section 14.2.2, the slope, b , of the least squares linear regression line of a plot of found 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 USATHAMA IRDMS (Section 10.4). The slope for the complete data set shall be used as the accuracy, even if the CRL was obtained from a truncated data set.

Estimates of accuracy cannot be calculated for Class 2 methods.



14.2.4 STANDARD DEVIATION

For Class 1, Class 1A, and Class 1B certification, the standard deviation, S, will be calculated at each target concentration according to:

$$(7) \quad \text{Standard Deviation} = S = \left[\frac{\sum Y_i^2 - \frac{(\sum Y_i)^2}{N}}{N - 1} \right]^{1/2}$$

where:

Y_i = The found concentration; and

N = Total number of Y values at each target concentration.

This calculation is performed by the USATHAMA software.

14.2.5 PERCENT INACCURACY

For Class 1, Class 1A, and Class 1B certification, the percent inaccuracy will be calculated at each target concentration according to:

$$(8) \quad \text{Percent Inaccuracy} = \frac{\bar{Y} - X}{X} (100)$$

where:

X = Target concentration; and

$\bar{Y}$ = Average found concentration at the target concentration.

This calculation is performed by the USATHAMA software.

14.2.6 PERCENT IMPRECISION

For Class 1, Class 1A, and Class 1B certification, the percent imprecision will be calculated at each target concentration according to:



$$(9) \quad \text{Percent Imprecision} = \frac{S}{\bar{Y}} (100)$$

where:

S = Standard deviation; and

$\bar{Y}$ = Average found concentration at the particular target concentration.

This calculation is performed by the USATHAMA software.

14.3 DOCUMENTATION

Upon completion of either precertification or certification performance testing, the Contractor Laboratory shall submit a Performance Data Package to the USATHAMA Chemistry Branch for review. For precertification, the contractor shall submit the following Precertification Performance Data Package:

- Precertification method description in USATHAMA format containing laboratory-specific information concerning preparation and analysis of precertification calibration standards (Appendix A);
- Chromatograms (low and high concentrations) if appropriate;
- Precertification calibration data, tabulation of concentration versus response (Appendix C);
- LOF and ZI test calculations and results for the precertification calibration curve (Appendices C and B);
- Certified calibration check standard(s) data (Class 1 and Class 1B only);
- Results of identification and purity analyses for all off-the-shelf reference materials (Section 8.3.3); and
- Checklist completed by the QAC (Appendix P).



For certification, the contractor shall submit the following Certification Performance Data Package:

- Final USATHAMA-approved copy of the Precertification Performance Data Package;
- Total method description in USATHAMA format containing approved deviations in the standardized method and laboratory-specific information concerning conduct of the method (Appendix A);
- Certification data, tabulation of found versus target concentration (Appendix C);
- LOF test calculations and results for the pooled data sets for found versus target concentrations (Appendices C and B);
- Linear regression, confidence bounds, reporting limit, accuracy, standard deviation, imprecision, and inaccuracy calculation results for the total data set and each sequential truncation, if performed (Appendix C);
- Narrative evaluation of effectiveness of the method for its intended use and shortfalls of the analytical method; and
- Checklist completed by the QAC (Appendix P).

In addition, the following should be included in the Certification Performance Data Package when applicable:

- Calibration data (initial and daily), tabulation of concentration versus response;
- Calibration curves (graphics with instrument response on the ordinate and concentration on the abscissa, not just the equation for the best fit calibration line) bracketing the tested range for each analyte (Section 8.1);
- Data and calculations demonstrating that the response for the Daily Calibration standard was within the required percentage (± 10 percent or ± 25 percent, depending on analysis type) of the response for the highest standard used during Precertification and Initial Calibration;
- For any chromatographic method, copies of the chromatograms from each day of certification analyses for the highest tested concentration and for the tested concentration closest to the CRL. In addition, one day's highest tested concentration chromatogram (so identified) will



have been allowed to run long enough to be able to identify any system peaks that may be present which, if unidentified, could result in compound mislabelling on subsequent chromatograms. Each chromatogram shall be labelled with the analysis date, analysis time, target concentration, test name, reference to the calibration curve used for quantification, and reference to the laboratory logbook where analytical activities were recorded. The identity of each peak shall also be labeled; and

- Mass spectra for all target analytes, surrogates, and tuning compounds.
- Explanation(s) for any manual integrations.
- All data sets when outlier replacement is used (Appendix Y).





15.0 CORRECTIVE ACTIONS

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 Project Manager, Analytical Task Manager, QAC, and analyst 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 should directly involve the Project Manager and the USATHAMA 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 analyst as a result of calibration checks and QC sample analyses.
- 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 routine to ensure analysis within allowed holding times;
 - Identifying vendors to supply reagents of sufficient purity; and
 - Revision of Contractor QA system or replacement of personnel.

For either immediate or long-term corrective actions, 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 must 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 needs to be performed and the results supplied with the weekly QC submittal as verification that the problem has been eliminated.



16.0 QUALITY ASSURANCE REPORTS TO MANAGEMENT

Normal submissions to USATHAMA include the Precertification and Certification Performance Data Packages (Section 14.3), IRDMS submissions (Section 10.6), audit reports (Section 12.0), and the results of QC activities (Section 11.0). When required in the task order, a CLP data package will also be submitted. During those periods when analyses are being conducted, all QC charts (tabular and graphical), as described in Section 11.4, must be submitted to the USATHAMA Chemistry Branch on a weekly basis. The QC report must be provided to the Chemistry Branch NLT 5 working days after analyses for a week are completed. Analysis date shall be defined by the day the analytical instrument was run (Section 10.3). 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 USATHAMA shall be utilized, when available. A checklist for inclusion with each control chart submission is shown in Appendix Q.

As an appendix to the project final report, the QAC, in coordination with the Analytical Task Manager and the Project Manager, shall 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 at 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 11.5;
- 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.



17.0 BIBLIOGRAPHY

American Chemical Society. 1980. "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry." Analytical Chemistry, Vol. 52, No. 14, pp. 2242-2249.

American Industrial Hygiene Association. Undated. Quality Control Manual: Quality Control for the Industrial Hygiene Laboratory. AIHA.

APHA-AWWA-WPCF. 1980. Standard Methods for the Examination of Water and Wastewater. 15th Edition, American Public Health Association, Washington, D.C.

ASTM. 1973. Biological Methods for the Assessment of Water Quality. Special Technical Publication (STP) 528, J. C. Cairns and K. L. Dickson, editors, Philadelphia, PA.

ASTM Standard Practice for Generation of Environmental Data Related To Waste Management Activities Quality Assurance/Quality Control. In Publication.

Barcelona, M. J., J. A. Helfrich, E. E. Garske and J. P. Gibb. 1984. "A Laboratory Evaluation of Ground Water Sampling Mechanisms." Ground Water Monitoring Review, Vol. 4, No. 2, pp. 32-41.

Bishop, T. A. "A Statistical View of Detection and Determination Limits in Chemical Analyses." Prepared for the Committee on Applications of Statistical Techniques in Chemical Problems, Battelle Columbus Laboratories, Columbus, OH.

Blank, L. T. 1980. Statistical Procedures for Engineering, Management, and Science, McGraw-Hill Book Company, New York, NY.

Currie, L. 1968. "Limits for Qualitative Detection and Quantitative Determination." Analytical Chemistry, Vol. 40, No. 3, pp. 586-593.

Federal Register, Part III. December 3, 1979. "Guidelines Establishing Test Procedures for the Analysis of Pollutants." Vol. 44, No. 233, pp. 69464- 69575.

Federal Register, Part III. November 29, 1983. "Toxic Substances Control; Good Laboratory Practice Standards." Vol. 48, No. 230, pp. 53922-53944.

Federal Register, Part VIII. October 26, 1984. "Guidelines Establishing Test Procedures for Analysis of Pollutants Under the Clean Water Act." Vol. 49, No. 209, pp. 43234-43442.

Hubaux, A., and G. Vos. 1970. "Decision and Detection Limits for Linear Calibration Curves." Analytical Chemistry, Vol. 42, No. 8, pp. 849-855.



Kirchmer, C. J. 1983. "Quality Control in Water Analyses." Environmental Science and Technology, Vol. 17, No. 4, pp. 174A-181A.

Kratochvil, B., and J. K. Taylor. 1981. "Sampling for Chemical Analysis." Analytical Chemistry, Vol. 53, No. 8, pp. 924A-938A.

Natrella, M. G. 1963. Experimental Statistics. NBS Handbook 91, National Bureau of Standards, Washington, DC.

Nielson, D. M., and G. L. Yeates. 1985. "A Comparison of Sampling Mechanisms Available for Small-Diameter Ground Water Monitoring Wells." Ground Water Monitoring Review, Vol. 5, No. 2, pp. 83-99.

Scheffe, Henry. 1959. The Analysis of Variance. John Wiley and Sons, Inc., New York, NY, pp. 426-427.

Snedecor, G. W., and W. G. Cochran. 1980. Statistical Methods. 7th Edition, Iowa State University Press, Ames, IA.

Taylor, J. K. 1981. "Quality Assurance of Chemical Measurements." Analytical Chemistry, Vol. 53, No. 14, pp. 1588A-1596A.

USATHAMA. 1983. Geotechnical Requirements for Drilling, Monitor Wells, Data Acquisition, and Reports. Aberdeen Proving Ground, MD.

U.S. Department of Health and Human Services Public Health Service Centers for Disease Control, National Institute for Occupational Safety and Health Division of Training and Manpower Development. Industrial Hygiene Laboratory Quality Control - 587- January 1980.

U.S. EPA. 1973. Biological Field and Laboratory Methods for Measuring the Quality of Surface Waters and Effluents. EPA-670/4-73-001, Environmental Research Center, Cincinnati, OH.

U.S. EPA. 1974. Development of Sample Preparation Methods for Analysis of Marine Organisms. EPA-660/3-74-026, Office of Research and Development, Washington, DC.

U.S. EPA. 1976. Quality Assurance Handbook for Air Pollution Measurement Systems: Volume I Principles. EPA-600/9-76-005, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC.

U.S. EPA. 1977a. NPDES Compliance Sampling Manual. Office of Water Enforcement, Washington, DC.

U.S. EPA. 1977b. Quality Assurance Handbook for Air Pollution Measurement Systems: Volume II - Ambient Air Specific Methods. EPA-600/4-77-027a, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC.



U.S. EPA. 1977c. Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III - Stationary Source Specific Methods. EPA-600/4-77-027b, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC.

U.S. EPA. 1978. Microbiological Methods for Monitoring the Environment. EPA-600/8-78-017, Environmental Monitoring and Support Laboratory, Cincinnati, OH.

U.S. EPA. 1979a. Handbook for Analytical Quality Control in Water and Wastewater Laboratories. EPA-600/4-79-019, Environmental Monitoring and Support Laboratory, Cincinnati, OH.

U.S. EPA. 1979b. Methods for Chemical Analysis of Water and Wastes. EPA- 600/4-79-020, Environmental Monitoring and Support Laboratory, Cincinnati, OH.

U.S. EPA. 1980a. Guidelines and Specifications for Preparing Quality Assurance Program Plans. QAMS-004/80, Office of Monitoring Systems and Quality Assurance, Washington, DC.

U.S. EPA. 1980b. Guidelines and Specifications for Preparing Quality Assurance Project Plans. MERL/QA-2, Municipal Environmental Research Laboratory, Cincinnati, OH.

U.S. EPA. 1980c. Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans. QAMS-005/80, Office of Monitoring Systems and Quality Assurance, Washington, DC.

U.S. EPA. 1980d. Samplers and Sampling Procedures for Hazardous Waste Streams. EPA-600/2-80-018, Municipal Environmental Research Laboratory, Cincinnati, OH.

U.S. EPA. 1982a. Handbook for Sampling and Sample Preservation of Water and Wastewater. EPA-600/4-82-029, Environmental Monitoring and Support Laboratory, Cincinnati, OH.

U.S. EPA. 1982b. NEIC Policies and Procedures. EPA-330/9-78-001-R, National Enforcement Investigations Center, Denver, CO.

U.S. EPA. 1982c. Quality Assurance Manual for the Environmental Sciences Research Laboratory. ESQA-002/82, Environmental Sciences Research Laboratory, Research Triangle Park, NC.

U.S. EPA. 1982d. Technical Enforcement Guidance: Groundwater Monitoring Assessment Programs at Interim Status Facilities. SW-954, Office of Solid Waste and Emergency Response, Washington, DC.

U.S. EPA. 1982e. Test Methods for Evaluating Solid Waste: Physical/ Chemical Methods. SW-846, Third Edition, Office of Solid Waste and Emergency Response, Washington, DC.

U.S. EPA. 1982f. Test Methods: Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater. EPA-600/4-82-057, Environmental Monitoring and Support Laboratory,



Cincinnati, OH.

U.S. EPA. 1982g. Test Methods: Technical Additions to Methods for Chemical Analysis of Water and Wastes. EPA-600/4-82-055, Environmental Monitoring and Support Laboratory, Cincinnati, OH.

U.S. EPA. 1983a. "Calculation of Data Quality Indicators." Office of Research and Development, Washington, DC.

U.S. EPA. 1983b. Preparation of Soil Sampling Protocol: Techniques and Strategies. EPA-600/4-83-020, Environmental Monitoring Systems Laboratory, Las Vegas, NV.

U.S. EPA. 1983c. Quality Assurance Handbook for Air Pollution Measurement Systems: Volume IV Meteorological Measurements. EPA-600/4-82-060, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC.

U.S. EPA. 1983d. Quality Assurance Handbook for Air Pollution Measurement Systems: Volume V - Manual for Precipitation Measurement Systems. EPA 600/4-82-042a and b, Environmental Monitoring Systems Laboratory, Research Triangle Park, NC.

U.S. EPA. 1984a. Characterization of Hazardous Waste Sites - A Methods Manual: Volume II - Available Sampling Methods, Second Edition. EPA 600/4-84-076, Environmental Monitoring Systems Laboratory, Las Vegas, NV.

U.S. EPA. 1984b. Remedial Investigations Guidance Document. Office of Emergency and Remedial Response, Washington, DC.

U.S. EPA. 1984c. Soil Sampling Quality Assurance User's Guide. EPA 600/4-84-043, Environmental Monitoring Systems Laboratory, Las Vegas, NV.

U.S. EPA. December 1986. Users Guide to the Contract Laboratory Program. Office of Emergency and Remedial Response, Washington, DC 20460.

U.S. Geological Survey. 1977a. Techniques of Water-Resources Investigations of the United States Geological Survey: Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples. Book 5, Chapter A4, U.S. Department of the Interior, Washington, DC.

U.S. Geological Survey. 1977b and subsequent revisions. National Handbook of Recommended Methods for Water-Data Acquisition. Office of Water Data Coordination, Reston, VA.

Wernimont, G. T. 1985. Use of Statistics to Develop and Evaluate Analytical Methods. AOAC.



Weston, A. G. 1984. "Obtaining Reliable Priority - Pollutant Analyses." Chemical Engineering, Vol. 91, No. 9, pp. 54-60.

Wilson, A. L. 1970. "The Performance Characteristics of Analytical Methods - I and II." Talanta, Vol. 17, pp. 21-44.

Youden, W. J. 1964. Statistical Methods for Chemists. John Wiley and Sons, New York, NY.





18.0 GLOSSARY

Accuracy -- Difference between individual analytical measurements and the true value, corresponding to the sum of systematic and random errors.

Analyte -- Chemical component for which analysis is conducted.

Analytical Method -- Set of written instructions completely defining the procedure to be adopted by the analyst in order to obtain an analytical result.

Audit -- Systematic check to determine the quality of operation of some function or activity. Audits may be of two basic types: 1) performance audits in which quantitative data are independently obtained for comparison with routinely obtained data in a measurement system; or 2) system audits of a qualitative nature that consist of an onsite review of a laboratory's quality assurance system and physical facilities for sampling, calibration, and measurement.

Certification -- Approval by USATHAMA to use an analytical method for analysis of specific analytes following submission of a Performance Data Package. Four certification categories are possible.

Certified Reporting Limit (Method) -- Lowest level of analyte in the sample being analyzed which can be quantitatively differentiated from zero with 90 percent confidence using a complete, specific analytical method and for which precision and accuracy criteria are valid.

Certified Range -- The range in which all sample measurements must be made, starting at the Certified Reporting Limit and usually extending as high as the highest certified concentration.

Chain-of-Custody -- Formalized system of creating an accurate written record which can be used to trace the possession and handling of a sample from the moment of collection through analysis and introduction of data as evidence.

Chemical Calibration Curve -- Best-fit regression curve determined from a plot of response versus calibration standard concentration.

Chemical Calibration Standard -- Solutions containing known amounts of analytes, introduced directly into the instrument to obtain the response versus concentration relationship for each analyte.

Comparability -- Confidence with which one data set can be compared to another.

Confidence Limit -- One of the end points of an interval which has a specified probability of containing a given parameter or characteristic.



Contractor Laboratory -- Analytical chemistry laboratory performing analysis of environmental samples in support of a USATHAMA contract. The laboratory may be part of the organization holding the contract with USATHAMA (prime contractor) or may be subcontracted to the prime contractor.

Control Analyte -- Analyte spiked into a QC sample. Control analytes may consist of target and/or surrogate analytes from certification. Control charts are required for each control analyte.

Control Samples -- Samples introduced into the train of environmental samples as monitors on the performance of the analytical method (Section 7.2).

Data Validation -- Systematic process for reviewing a body of data against a set of criteria to provide assurance that the data are adequate for their intended use. Data validation consists of data editing, screening, checking, auditing, verification, certification, and review.

Data Quality -- Totality of features and characteristics of a data set that bears on its ability to satisfy a given purpose.

Development Laboratory -- Laboratory designated and/or contracted to develop an analytical method.

Field Blank -- Standard matrix sample, to which no analyte of interest has been added, that is transported to the sampling site and back, to ensure that no contamination is introduced during shipment. This sample may be opened near a sampling location or may be unopened, depending on the type of information desired. Another procedure for creating a field blank is to sample the distilled water used in the field, placing the sample in a randomly selected container.

Field Duplicate -- A second sample from one site taken in the field and submitted to the laboratory as a separate sample. It is usually analyzed "blind" by the laboratory, i.e., the laboratory does not know that it is a duplicate of another sample. The results act as an external check on the combined precision of sampling and analysis.

Found Concentration -- Concentration based on instrumental response of the sample compared to the instrument calibration curve.

Holding Time -- The maximum time allowable between sample collection and analysis.

IRDMS -- Installation Restoration Data Management System, a USATHAMA computerized data submittal, storage, and retrieval system.

Lot Size, Maximum -- Number of samples, including QC samples, that can be processed through a step of the analytical method during a single time period (not to exceed one day) as determined by time or by the equipment limiting step of the method.



Method Blank -- Standard matrix sample to which no analyte of interest has been added that is processed in the same manner as samples, to ensure that the apparatus and reagents used are not contributing contaminants to the analysis.

Method Performance Samples -- Spiked samples prepared in a standard matrix whose analytical results are used to prepare the Performance Data Package during certification activities.

Minimum Testing Range -- Smallest tested concentration range that may be used during Class 1, Class 1A, and Class 1B certification activities. This range is defined as spanning 0.5 to 10 times the Target Reporting Limit, including a blank.

Negative Interference -- A response indicating a lesser amount of analyte than actually present.

Outlier -- An extreme observation that is shown to have a low probability of belonging to a data population.

Percent Imprecision -- Single concentration standard deviation divided by the average found concentration; also called Relative Standard Deviation.

Percent Inaccuracy -- The difference between the found and target (true) concentration, divided by the target concentration and multiplied by 100.

Performance Data Package -- The complete set of method description, calibration curves, standard sample analysis data, and statistical treatment of sample data that is submitted to USATHAMA during method precertification and certification.

Positive Interference -- A response indicating the presence of an analyte in greater amounts than actually present.

Precision -- Degree of mutual agreement among individual measurements made under prescribed conditions with a single test procedure.

Project QC Plan -- An orderly assembly of detailed and specific procedures which delineates how data of known and accepted quality are produced for a specific project.

Project Officer -- The individual responsible for the project at USATHAMA. The Project Officer may be the USATHAMA Chemistry Branch Chemist assigned to the project or the Contract COR, depending on the contract under which work is being performed.

Quality Assurance (QA) -- The total integrated program for assuring and documenting the reliability of monitoring and measurement data and for integrating quality planning, quality assessment, and quality improvement efforts to meet user requirements.

Quality Control (QC) -- The routine application of procedures for obtaining prescribed standards of performance in the monitoring and measurement process.



Quality Control Sample -- Sample that is introduced into a train of environmental samples as a monitor on the performance of the analytical system.

Rank of an Observation -- The number assigned to an observation if a collection of observations is ordered from smallest to largest and each observation is given the number corresponding to its place in the order.

Recovery -- Difference between the analytical results before and after spiking, divided by known amount of spiking compound and multiplied by 100 to convert to percentage.

Representativeness -- The degree to which data accurately and precisely represent a characteristic of a populations parameter variations at a sampling point, a process condition, or an environmental condition.

Response Factor -- The change in the size of peaks of standards that are run under the same conditions. The areas and retention time of the standards should not vary.

Scientific Notation -- A method of expressing a number with the first significant digit to the left of the decimal point, the remaining significant digits to the right of the decimal point, and multiplied by ten raised to a positive or negative integer power.

Sensitivity -- Instrument response (counts, peak area, etc.) observed for the absolute quantity of analyte introduced into the instrument at the reporting limit.

Significant Figures -- The number of digits used to express a result in scientific notation. All digits are expected to be known definitely, except the last digit, which may be in doubt.

Spiked Sample -- A sample to which a known amount of analyte is added and which is then carried through the complete analytical method.

Standard Deviation -- The positive square root of the expected value of the square of the difference between a random variable and its mean.

Standard Sample -- Sample prepared in a standard matrix as defined in Sections 5.6.1 and 5.6.2.

Standing Operating Procedure (SOP) -- A written document which details an operation, analysis or action whose mechanisms are thoroughly prescribed and which is commonly accepted as the method for performing certain routine or repetitive tasks.

Target Analyte -- Specific, certified analyte reported for every sample analyzed by a given method.

Target Concentration -- Known spiked concentration.



Target Reporting Limit (TRL) -- Desired, required, or expected Method Reporting Limit estimated before performing certification analyses for the purpose of determining target concentrations during certification.

Tested Concentration -- One of the target concentrations used during analysis of Method Performance Samples.

Tested (Concentration) Range -- The range of concentrations used in preparing Method Performance Standards for certification activities.

Traceability -- The ability to completely reconstruct all activities from the time of sampling to data reporting, including all sample handling as well as instrument maintenance, QC results, and calibration curves.

Validity -- Degree to which the reported results represent that which they intend to represent.





19.0 LIST OF ACRONYMS

AAS -- Atomic Absorption Spectroscopy

ASTM -- American Society for Testing and Materials

BOD -- Biochemical Oxygen Demand

CLP -- Contract Laboratory Program

COD -- Chemical Oxygen Demand

CRL -- Certified Reporting Limit

EPA -- U.S. Environmental Protection Agency

GC -- Gas Chromatograph(y)

IC -- Ion Chromatograph(y)

ICAP -- Inductively Coupled Plasma-Emission Spectroscopy

IR -- Installation Restoration

IRDMS -- Installation Restoration Data Management System

IRM -- Interim Reference Material

LCL -- Lower Control Limit

LOF -- Lack of Fit

LWL -- Lower Warning Limit

MS -- Mass Spectroscopy

MTR -- Minimum Testing Range

NIST -- National Institute of Standards and Technology

NMR -- Nuclear Magnetic Resonance

QA -- Quality Assurance



QAC -- Quality Assurance Coordinator

QC -- Quality Control

SARM -- Standard Analytical Reference Material

SRM -- Standard Reference Material from NIST

TDS -- Total Dissolved Solids

TOC -- Total Organic Carbon

TSS -- Total Suspended Solids

TRL -- Target Reporting Limit

UCL -- Upper Control Limit

USATHAMA -- U.S. Army Toxic and Hazardous Materials Agency

UWL -- Upper Warning Limit

ZI -- Zero Intercept



APPENDIX A

FORMAT FOR DOCUMENTATION OF ANALYTICAL METHODS





APPENDIX A

FORMAT FOR DOCUMENTATION OF ANALYTICAL METHODS PRECERTIFICATION CALIBRATION

TITLE

I. SUMMARY

- A. ANALYTE(S). State analyte(s) that can be analyzed by this method (e.g., 246TNT).
- B. MATRIX. Environmental matrix (or matrices) for which the method is applicable (e.g., groundwater and surface water).
- C. GENERAL METHOD. Brief method description (e.g., direct injection HPLC with UV detection).

II. APPLICATION

- A. CALIBRATION RANGE. Concentration range of the calibration standards (representative of the extract).
- B. TESTED CONCENTRATION RANGE. Based upon the procedure, the calculated equivalent tested concentration range in the original matrix (e.g., 1 - 20 ug/L in water).
- C. SENSITIVITY. Instrumental response observed for absolute quantity of analyte at the calculated target limit (e.g., 1500 area units for 40 picograms).
- D. INTERFERENCES. Any observed interferences or any interferences anticipated based on the method of analysis.
- E. SAFETY INFORMATION. Special health hazards and safety precautions for handling samples, solutions, and chemicals.

III. APPARATUS AND CHEMICALS

- A. INSTRUMENTATION. Makes and models of instruments and associated components. Operating parameters of instruments and associated components. Retention times and retention time windows.



B. ANALYTES. Chemical Abstracts Service registry number and basic physical properties.

C. REAGENTS, SARMS AND STANDARDS. Identity, concentration, purity, and source of reagents and SARMS. Traceability (where applicable).

IV. PRECERTIFICATION CALIBRATION

A. PREPARATION OF STANDARDS. Step-by-step preparation procedures, including proper storage, shelf-life, and concentrations.

B. INSTRUMENT CALIBRATION. Detailed procedures for instrument tuning and analysis of standards.

C. Analysis of Calibration Data. Criteria for acceptability.

V. PROCEDURE

A. SEPARATIONS.

B. CHEMICAL REACTIONS.

C. INSTRUMENTAL ANALYSIS.

D. CONFIRMATIONAL ANALYSIS (if applicable).

VI. CALCULATIONS. Detailed procedure for calculating sample concentrations from the instrument responses, including calibration curves and formulae.

VII. REFERENCES. Published references for the procedures described.

VIII. DATA

A. Response versus concentration data.

B. Response versus concentration graphs.

C. LOF Tests.

D. ZI Tests.

E. Chromatograms (where applicable).



January 1990

USATHAMA PAM 11-41

Revision No. 0

F. Results of Check Standards



FORMAT FOR DOCUMENTATION OF ANALYTICAL METHODS
CERTIFICATION

METHOD NO. _____

TITLE

I. SUMMARY

- A. ANALYTE(S). State analyte(s) that can be analyzed by this method (e.g., 246TNT).
- B. MATRIX. Environmental matrix (or matrices) for which the method is applicable (e.g., groundwater and surface water).
- C. GENERAL METHOD. Brief method description (e.g., direct injection HPLC with UV detection).

II. APPLICATION

- A. TESTED CONCENTRATION RANGE. Tested concentration range in the original matrix (e.g., 1 - 20 ug/L in water).
- B. SENSITIVITY. Instrumental response observed for absolute quantity of analyte at the calculated reporting limit (e.g., 1500 area units for 40 picograms).
- C. REPORTING LIMIT. Certified reporting limit for complete analytical method determined from found versus actual concentrations for spiked standard matrix samples and calculated according to USATHAMA reporting limit program, expressed in terms of concentration in original matrix.
- D. INTERFERENCES. Any observed interferences or any interferences anticipated based on the method of analysis.
- E. ANALYSIS RATE. Estimated maximum number of samples that can be analyzed by this method in an 8-hour day after instrument calibration.
- F. SAFETY INFORMATION. Special health hazards and safety precautions for handling samples, solutions, and chemicals.



III. APPARATUS AND CHEMICALS

- A. GLASSWARE/HARDWARE. Quantities and sizes of all miscellaneous equipment, including sources of specialty or trademark items.
- B. INSTRUMENTATION. Makes and models of instruments and associated components. Operating parameters of instruments and associated components. Retention times and retention time windows (to include the criteria used in setting the retention time windows).
- C. ANALYTES. Chemical Abstracts Service registry number and basic physical properties.
- D. REAGENTS AND SARMS. Identity, concentration, purity, and source of reagents and SARMS. Traceability (where applicable).

IV. CALIBRATION

A. INITIAL CALIBRATION

- 1. PREPARATION OF STANDARDS. Step-by-step preparation procedures, including proper storage, shelf-life, and concentrations.
- 2. INSTRUMENT CALIBRATION. Detailed procedures for instrument tuning and analysis of standards.
- 3. ANALYSIS OF CALIBRATION DATA. Criteria for acceptability, based on precertification calibration curve.

B. DAILY CALIBRATION

- 1. PREPARATION OF STANDARDS. Step-by-step preparation procedures, including proper storage, shelf-life, and concentrations.
- 2. INSTRUMENT CALIBRATION. Detailed procedures for instrument tuning and analysis of standards.
- 3. ANALYSIS OF CALIBRATION DATA. Criteria for acceptability.
- 4. CALIBRATION CHECKS. As used internally by laboratory and/or specified by this QA Program.



V. CERTIFICATION TESTING. Control spikes. Step-by-step procedure for preparing standard matrix certification samples.

VI. SAMPLE HANDLING AND STORAGE

A. SAMPLING PROCEDURE. Special considerations due to the nature of the analyte; required preservation procedures.

B. CONTAINERS.

C. STORAGE CONDITIONS. Conditions required in the field and the laboratory to maintain sample integrity.

D. HOLDING TIME LIMITS.

E. SOLUTION VERIFICATION. Description of measures to verify integrity of working calibration and control spike solutions.

VII. PROCEDURE

A. SEPARATIONS.

B. CHEMICAL REACTIONS.

C. INSTRUMENTAL ANALYSIS.

D. CONFIRMATIONAL ANALYSIS (if applicable).

VIII. CALCULATIONS. Detailed procedure for calculating sample concentrations from the instrument responses, including calibration curves, and formulae.

IX. DAILY QUALITY CONTROL

A. CONTROL SAMPLES. Detailed, step-by-step procedure for preparing spiked QC samples, including spiking concentrations based on certified reporting limit.

B. CONTROL CHARTS. Description of charts to be maintained. List initial warning and control limits as obtained from certification data.

X. REFERENCES. Published references for the procedures described. Major deviations from referenced method(s) summarized.

XI. DATA



A. OFF-THE-SHELF ANALYTICAL REFERENCE MATERIALS CHARACTERIZATION.

B. INITIAL CALIBRATION

1. Response versus concentration data.
2. Response versus concentration graphs.

C. DAILY CALIBRATION

1. Response.
2. Required percentage or two standard deviation limits.

D. STANDARD CERTIFICATION SAMPLES

1. Tabulation and graph of found versus target concentrations.
2. LOF and ZI tests for the pooled data.
3. Calculated least squares linear regression line, confidence bounds, reporting limit, accuracy, standard deviation, percent imprecision, and percent inaccuracy, as shown in Appendix C.
4. Chromatograms from each day of certification analyses for the highest tested concentration and for the tested concentration closest to the calculated reporting limit. Each chromatogram shall be labeled with the analysis date, analysis time, target concentration, test name, reference to the calibration curve used for quantification, and reference to the laboratory logbook where analytical activities were recorded. The identity of each peak shall also be labeled. At least one chromatogram for the highest tested concentration will be allowed to proceed at least double the retention time of the last eluting compound in order to determine if any system peaks are present.
5. Results of check standards.
6. Summary table of method certification table parameters.



APPENDIX B

LACK OF FIT AND ZERO INTERCEPT TESTS



APPENDIX B

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:

$$Y = Y_0 + bX$$

where:

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

Y_0 = Y Axis Intercept;

b = Slope of the Line; and

X = Target Concentration.

The estimates Y_0 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:



$$\hat{Y} = b_0 X$$

where:

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

b_0 = Slope of Line Through Origin; and

X = Target Concentration.

The estimate of b_0 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:

$$b = \frac{N \sum X_i Y_i - \sum X_i \sum Y_i}{N \sum X_i^2 - (\sum X_i)^2} \quad Y_0 = \frac{\sum Y_i - b \sum X_i}{N}$$

For the model through the origin:

$$b_0 = \frac{\sum X_i Y_i}{\sum X_i^2} \quad Y_0 = 0$$

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:

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

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:

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

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:

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

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:

$$\text{SS LOF} = (\text{SS Residual}) - (\text{Total SS Random Error})$$

Similarly, the df associated with LOF is given by:

$$\text{df LOF} = (\text{df Residual}) - (\text{df Total Random Error})$$

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 B-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 B-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 B.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	$\left[\sum Y^2 - \frac{(\sum Y)^2}{N} \right] - b^2 \left[\sum X^2 - \frac{(\sum X)^2}{N} \right]$	N-2	$\frac{\text{Residual SS}}{N-2}$	-
Individual Error (for each set of data at each concentration)	$\sum Y^2 - \frac{(\sum Y)^2}{n}$ (for duplicates -- $\frac{\sum d^2}{2}$)	n-1	-	-
Total Error	$\sum \text{Individual Error SS}$	$\sum \text{df for Individual Error}$	$\frac{\text{Total Error SS}}{\text{df Total Error}}$	-
Lack of Fit (LOF)	Residual SS - Total Error SS	df Residual - df Total Error	$\frac{\text{LOF SS}}{\text{df LOF}}$	$\frac{\text{MS LOF}}{\text{MS Total Error}}$

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 B.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.

$\alpha = 0.05$

$\nu_1 \backslash \nu_2$	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.



B.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 B-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 B-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 B.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	$\frac{\text{Residual SS}}{N-1}$	-
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	$\Sigma \text{ Individual Error SS}$	$\Sigma \text{ df for Individual Error}$	$\frac{\text{Total Error SS}}{\text{df Total Error}}$	-
Lack of Fit (LOF)	Residual SS - Total Error SS	df Residual - df Total Error	$\frac{\text{LOF SS}}{\text{df LOF}}$	$\frac{\text{MS LOF}}{\text{MS Total Error}}$

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.



B.3 EXAMPLE STATISTICAL ANALYSIS

The following pages contain examples of LOF/ZI testing for a calibration curve (Tables B-4 and B-5) and for certification data (Table B-6). The calculations shall be performed by the computer software supplied by USATHAMA and submitted with the appropriate Precertification or Certification Performance Data Packages.



Table B-4. STATISTICAL ANALYSIS OF CALIBRATION DATA
FOR SPECTROPHOTOMETRIC ANALYSIS OF MERCURY IN WATER

PRE-CERTIFICATION ANALYSIS

Report Date: 11/07/89

Page: 1

Method Name: METALS/WATER/CVAA
Compound: HG
Units of Measure: UGL

Laboratory: TH
Analysis Date: 11/07/89
Matrix: WA

ANALYSIS OF RESIDUAL VARIATIONS

--- Model with Intercept --- - Model through the Origin -
 $Y = (0.004760922) + (0.098740291)X$ $Y = (0.099416507)X$

	(SS)	(df)	(MS)	(SS)	(df)	(MS)
Residual:	0.000820763	8	0.000102595	0.000928309	9	0.000103145
Total Error:	0.000700500	5	0.000140100	0.000700500	5	0.000140100
Lack of Fit:	0.000120263	3	0.000040088	0.000227809	4	0.000056952

LOF F-Ratio(F): 0.286136926
Critical 95% F: 5.41

LOF F-Ratio(F): 0.406511458
Critical 95% F: 5.19

ZERO INTERCEPT HYPOTHESIS

Zero Intercept Accepted

Calculated F: 1.048250227 Critical 95% F: 5.32

TABLE OF DATA POINTS

Targets: 5

Measures per Target: 2

	Target Value	Instrument Values	
1:	0.5000000	0.0540000	0.0500000
2:	1	0.1030000	0.1090000
3:	2	0.2020000	0.1950000
4:	5	0.4940000	0.5140000
5:	10	0.9750000	1.0050000

*** END OF PRE-CERTIFICATION DATA TABLE ***



Table B-5. STATISTICAL ANALYSIS OF CALIBRATION DATA
FOR SPECTROPHOTOMETRIC ANALYSIS OF SELENIUM IN WATER

PRE-CERTIFICATION ANALYSIS

Report Date: 11/07/89

Page: 1

Method Name: METALS/WATER/GFAA
Compound: SE
Units of Measure: UGL

Laboratory: TH
Analysis Date: 11/07/89
Matrix: WA

ANALYSIS OF RESIDUAL VARIATIONS

--- Model with Intercept --- - Model through the Origin -
Y = (0.005165858) + (0.090982201)X Y = (0.091715931)X

	(SS)	(df)	(MS)	(SS)	(df)	(MS)
Residual:	0.004172361	8	0.000521545	0.004298979	9	0.000477664
Total Error:	0.000726000	5	0.000145200	0.000726000	5	0.000145200
Lack of Fit:	0.003446361	3	0.001148787	0.003572979	4	0.000893245

LOF F-Ratio(F): 7.911755831 LOF F-Ratio(F): 6.151823158
Critical 95% F: 5.41 Critical 95% F: 5.19
Data Not Linear Data Not Linear

ZERO INTERCEPT HYPOTHESIS

** Models not linear. Do not test Zero Intercept hypothesis.

Diagnose and correct analytical system before continuing.

TABLE OF DATA POINTS

Targets: 5

Measures per Target: 2

	Target Value	Instrument Values	
1:	0.5000000	0.0540000	0.0500000
2:	1	0.1030000	0.1090000
3:	2	0.2020000	0.1920000
4:	5	0.4140000	0.4340000
5:	10	0.9150000	0.9450000

*** END OF PRE-CERTIFICATION DATA TABLE ***



Table B-6. STATISTICAL ANALYSIS OF CERTIFICATION DATA
FOR SPECTROPHOTOMETRIC ANALYSIS OF CHROMIUM IN WATER

CERTIFICATION ANALYSIS

Report Date: 11/07/89

Method Name: METALS/WATER/ICP
Compound: CR
Units of Measure: UGL

Laboratory: TH
Analysis Date: 11/07/89
Matrix: WA

ANALYSIS OF RESIDUAL VARIATIONS

--- Model with Intercept --- - Model through the Origin -
Y = (0.034223301) + (1.000323620)X Y = (1.000863720)X

	(SS)	(df)	(MS)	(SS)	(df)	(MS)
Residual:	9.047402910	18	0.502633495	9.058517270	19	0.476764067
Total Error:	7.632500000	15	0.508833333	7.632500000	15	0.508833333
Lack of Fit:	1.414902910	3	0.471634303	1.426017270	4	0.356504318

LOF F-Ratio(F): 0.926893488 LOF F-Ratio(F): 0.700630824
Critical 95% F: 3.29 Critical 95% F: 3.06

ZERO INTERCEPT HYPOTHESIS

Zero Intercept Accepted Calculated F: 0.022112255 Critical 95% F: 4.41

TABLE OF DATA POINTS

Targets: 5

Measures per Target: 4

Target Value Found Concentration

1:	4.5000000	3.8000000	4.7000000	4.1000000	4.3000000
2:	9	9.2000000	8.9000000	8.8000000	8.7000000
3:	18	19.1000000	18.3000000	17.9000000	18.2000000
4:	45	44.4000000	46	45.7000000	45.3000000
5:	90	88.6000000	89	91.2000000	90.7000000

*** END OF CERTIFICATION LACK OF FIT DATA TABLE ***



APPENDIX C

SAMPLE OUTPUT OF USATHAMA STATISTICAL ANALYSIS PROGRAM
REQUIRED FOR PRECERTIFICATION/CERTIFICATION





APPENDIX C

SAMPLE OUTPUT OF USATHAMA STATISTICAL ANALYSIS PROGRAM REQUIRED FOR PRECERTIFICATION/CERTIFICATION

The following pages contain output from the statistical analysis computer software supplied by USATHAMA. The calculations and tables shown here shall be submitted as part of the Precertification and Certification Performance Data Packages for Class 1, Class 1A, and Class 1B methods. Data submitted with the Performance Data Package shall conform to the sample format shown herein; all required calculations and tables must be provided.

The enclosed output was obtained from the most current USATHAMA computer software available. Modifications to the program shall take precedence over the output shown herein.



PRE-CERTIFICATION ANALYSIS

Report Date: 11/06/89

Page: 1

Method Name: EXAMPLE
 Compound: TEST
 Units of Measure: UGL

Laboratory: TH
 Analysis Date: 11/06/89
 Matrix: WA

ANALYSIS OF RESIDUAL VARIATIONS

--- Model with Intercept --- - Model through the Origin -
 $Y = (3.734532290) + (1001.336550)X$ $Y = (1003.447870)X$

	(SS)	(df)	(MS)	(SS)	(df)	(MS)
Residual:	164.9304260	8	20.61630325	235.6420900	9	26.18245444
Total Error:	49.50000000	5	9.900000000	49.50000000	5	9.900000000
Lack of Fit:	115.4304260	3	38.47680867	186.1420900	4	46.53552250

LOF F-Ratio(F): 3.886546330
 Critical 95% F: 5.41

LOF F-Ratio(F): 4.700557828
 Critical 95% F: 5.19

ZERO INTERCEPT HYPOTHESIS

Zero Intercept Accepted

Calculated F: 3.429890565 Critical 95% F: 5.32

TABLE OF DATA POINTS

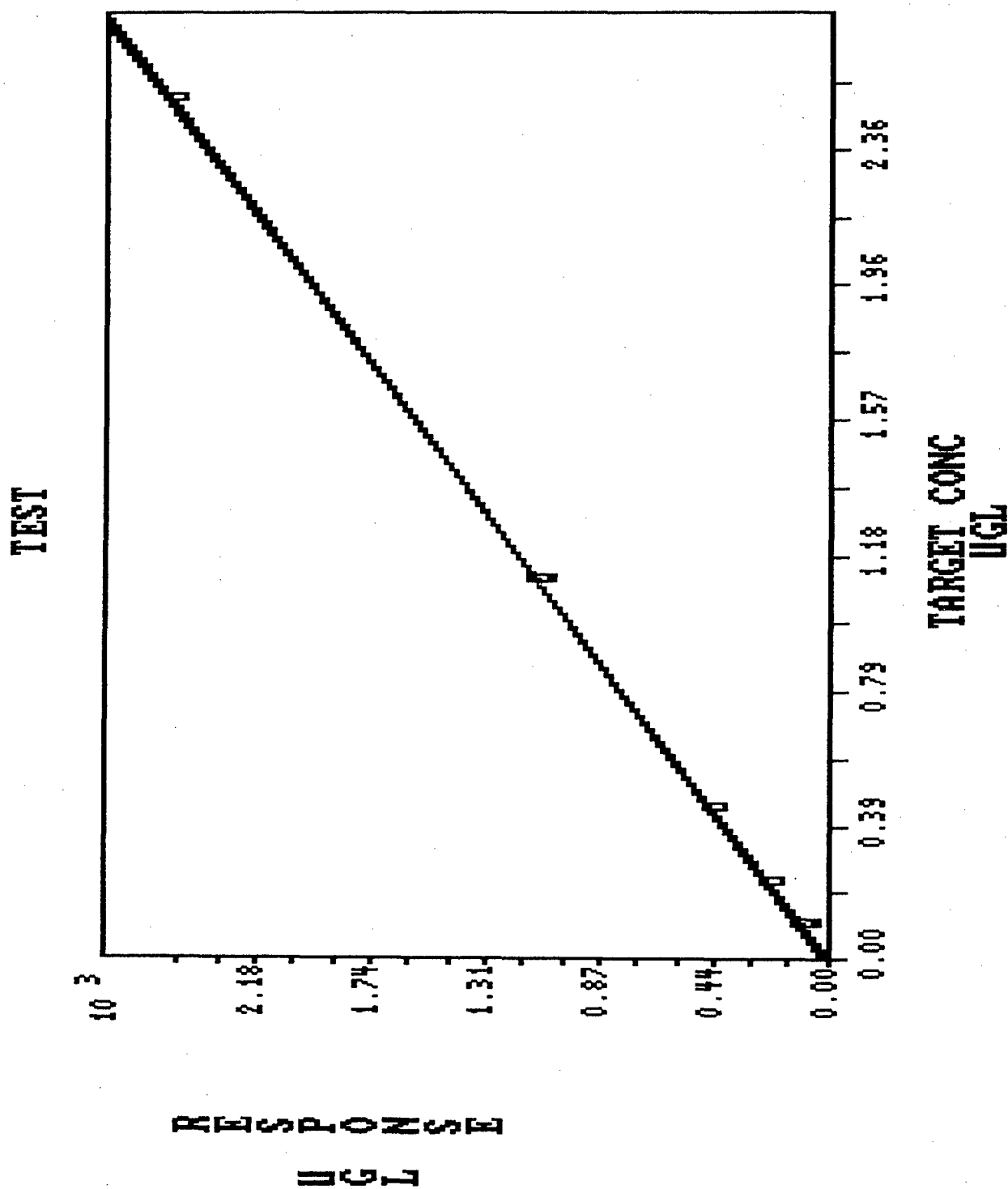
Targets: 5

Measures per Target: 2

	Target Value	Instrument Values	
1:	0.1000000	102	99
2:	0.2200000	223	225
3:	0.4400000	441	447
4:	1.1000000	1109	1114
5:	2.5000000	2502	2507

*** END OF PRE-CERTIFICATION DATA TABLE ***





Revision No. 0

CERTIFICATION ANALYSIS

Report Date: 11/06/89

Method Name: EXAMPLE
 Compound: TEST
 Units of Measure: UGL

Laboratory: TH
 Analysis Date: 11/06/89
 Matrix: WA

ANALYSIS OF RESIDUAL VARIATIONS

--- Model with Intercept --- - Model through the Origin -
 $Y = (0.037863471) + (0.897710724)X$ $Y = (0.922155819)X$

	(SS)	(df)	(MS)	(SS)	(df)	(MS)
Residual:	0.078619297	18	0.004367739	0.092223765	19	0.004853882
Total Error:	0.071763000	15	0.004784200	0.071763000	15	0.004784200
Lack of Fit:	0.006856297	3	0.002285432	0.020460765	4	0.005115191

LOF F-Ratio(F): 0.477704158
 Critical 95% F: 3.29

LOF F-Ratio(F): 1.069184263
 Critical 95% F: 3.06

ZERO INTERCEPT HYPOTHESIS

Zero Intercept Accepted

Calculated F: 3.114762493 Critical 95% F: 4.41

TABLE OF DATA POINTS

Targets: 5

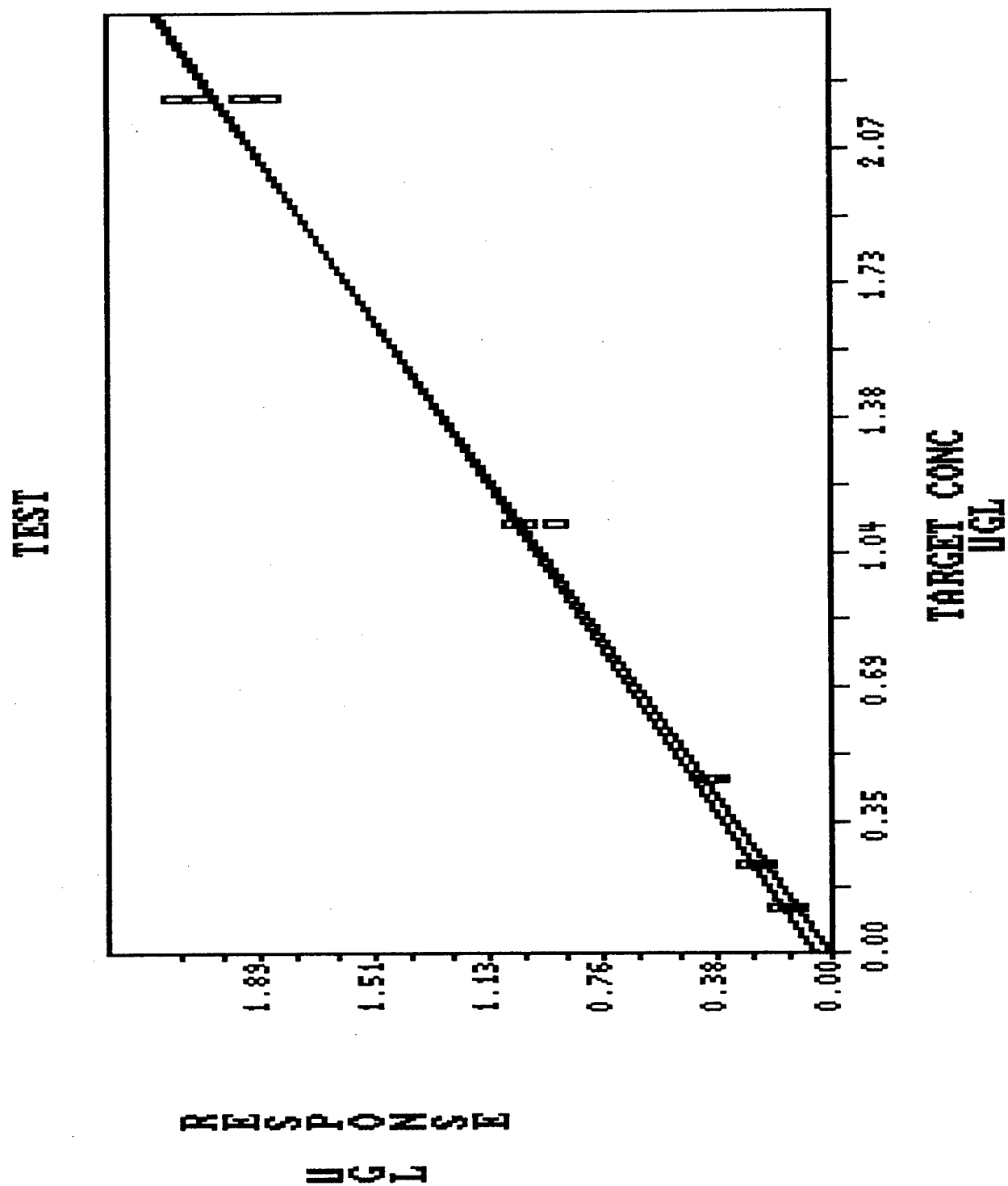
Measures per Target: 4

Target Value Found Concentration

1:	0.1100000	0.1800000	0.1360000	0.1390000	0.1520000
2:	0.2200000	0.2800000	0.2460000	0.2480000	0.2390000
3:	0.4400000	0.4200000	0.3850000	0.3970000	0.4110000
4:	1.1000000	1.0300000	1.0300000	1.0670000	0.9200000
5:	2.2000000	2.0900000	1.8650000	2.1760000	1.9610000

*** END OF CERTIFICATION LACK OF FIT DATA TABLE ***





CERTIFICATION ANALYSIS

Report Date: 11/06/89

Method Name: EXAMPLE
Compound: TEST
Units of Measure: UGL

Laboratory: TH
Analysis Date: 11/06/89
Matrix: WA

TABLE OF RESULTS FOR TRUNCATED DATA SET

Target Concentration	Standard Deviation	Percent Inaccuracy	Percent Imprecision
0.1100000	0.0200728	37.954545	13.227535
0.2200000	0.0182460	15.113636	7.2047400
0.4400000	0.0154137	-8.352273	3.8223778
1.1000000	0.0636049	-8.022727	6.2866222
2.2000000	0.1374845	-8.045455	6.7960724



CERTIFICATION ANALYSIS

Report Date: 11/06/89

Method Name: EXAMPLE
Compound: TEST
Units of Measure: UGL

Laboratory: TH
Analysis Date: 11/06/89
Matrix: WA

TABLE OF DATA POINTS

Target Concentration	Found Concentration
0	0 0 0 0
0.1100000	0.1800000 0.1360000 0.1390000 0.1520000
0.2200000	0.2800000 0.2460000 0.2480000 0.2390000
0.4400000	0.4200000 0.3850000 0.3970000 0.4110000
1.1000000	1.0300000 1.0300000 1.0670000 0.9200000
2.2000000	2.0900000 1.8650000 2.1760000 1.9610000



CERTIFICATION ANALYSIS

Report Date: 11/06/89

Method Name: EXAMPLE
Compound: TEST
Units of Measure: UGL

Laboratory: TH
Analysis Date: 11/06/89
Matrix: WA

-- REGRESSION EQUATION --
 $Y = 0.9049594X + 0.0266359$

-- UPPER REPORTING LIMIT --
2.2000000

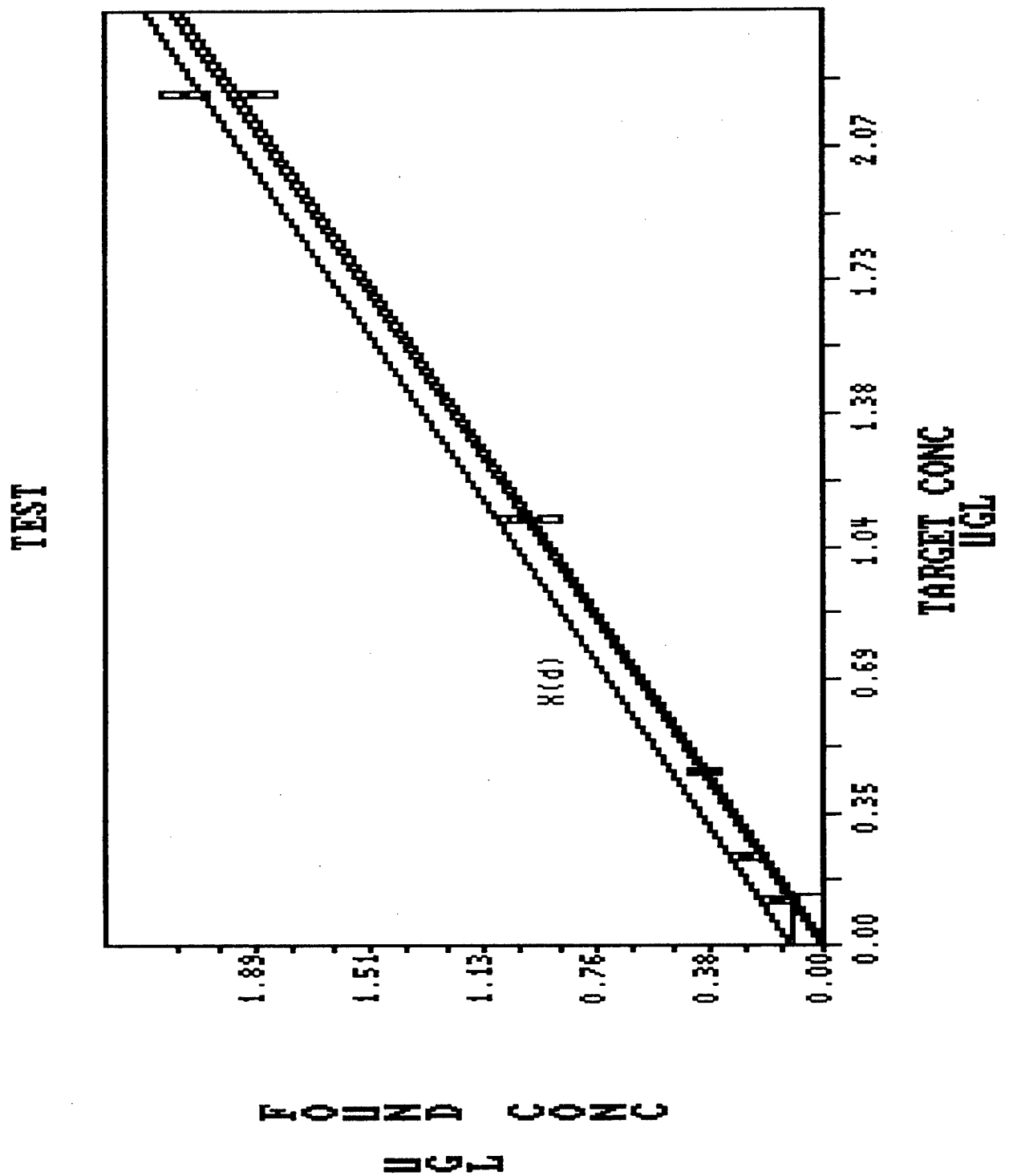
-- SLOPE --
0.9049594

SUMMARY TRUNCATION TABLE

Target Concentrations Used	Slope	% Change from Total Data Set	% Change from Previous Data Set
Entire data set	0.9049594	0	0
minus 1 highest	0.8919376	1.4389388	1.4389388
minus 2 highest	0.8901948	1.6315183	0.1953911

Target Concentrations Used	Certified Reporting Limit	Upper Reporting Limit
Entire data set	0.2410763	2.2000000
Minus 1 highest	0.1525508	2.2000000
Minus 2 highest	0.1300442	2.2000000







APPENDIX D

DOCUMENTATION FOR PROPOSED METHOD DEVELOPMENT





APPENDIX D

DOCUMENTATION FOR PROPOSED METHOD DEVELOPMENT

1. Organization submitting documentation.
2. Statement of the problem.
3. Description of the technical approach to include specific details on procedures, solvents, instrumentation, etc.
4. Estimate of resources required to include labor hours, funds, and schedule.





APPENDIX E

RANK SUM TEST





APPENDIX E

RANK SUM TEST

The following pages contain examples of the Rank Sum Test used for evaluating Class 2 certification performance data. The calculations are not performed by the computer software supplied by USATHAMA. The Rank Sum Test calculations shall be submitted as part of the Certification Performance Data Package for Class 2 methods.

Table E-1. Rank Sum Test, Example 1

<u>Standard Sample</u>	<u>Results</u>	<u>Rank</u>	<u>Average Rank</u>
Blank	NN	1	2.5
Blank	NN	2	2.5
Blank	NN	3	2.5
Blank	NN	4	2.5
Spike	PP	5	6.5
Spike	PP	6	6.5
Spike	PP	7	6.5
Spike	PP	8	6.5

NN = Negative; PP = Positive

$$\text{Average Rank for Negative Results} = \frac{1 + 2 + 3 + 4}{4} = 2.5$$

$$\text{Average Rank for Positive Results} = \frac{5 + 6 + 7 + 8}{4} = 6.5$$

$$\text{Sum of Average Ranks for Blanks} = 2.5 + 2.5 + 2.5 + 2.5 = 10.$$

The criterion for acceptability is that the sum of the average ranks of blanks be less than or equal to 10. Therefore, the certification is acceptable.



Table E-2. Rank Sum Test, Example 2

<u>Standard Sample</u>	<u>Results</u>	<u>Rank</u>	<u>Average Rank</u>
Blank	NN	1	2
Blank	NN	2	2
Blank	NN	3	2
Blank	PP	4	6
Spike	PP	5	6
Spike	PP	6	6
Spike	PP	7	6
Spike	PP	8	6

NN = Negative; PP = Positive

Average Rank for Negative Results = $\frac{1 + 2 + 3}{3} = 2$

Average Rank for Positive Results = $\frac{4 + 5 + 6 + 7 + 8}{5} = 6$

Sum of Average Ranks for Blanks = $2 + 2 + 2 + 6 = 12$.

Because the sum of the average ranks of blanks exceed the criterion of less than or equal to 10, the results are unacceptable, therefore,

Test an additional two blanks and two spikes:

<u>Standard Sample</u>	<u>Results</u>	<u>Rank</u>	<u>Average Rank</u>
Blank	NN	1	3
Blank	NN	2	3
Blank	NN	3	3
Blank-New	NN	4	3
Blank-New	NN	5	3
Blank	PP	6	9
Spike	PP	7	9
Spike	PP	8	9
Spike	PP	9	9
Spike	PP	10	9
Spike-New	PP	11	9
Spike-New	PP	12	9



$$\text{Average Rank for Negative Results} = \frac{1 + 2 + 3 + 4 + 5}{5} = 3$$

$$\text{Average Rank for Positive Results} = \frac{6 + 7 + 8 + 9 + 10 + 11 + 12}{7} = 9$$

$$\text{Sum of Average Ranks for Blanks} = 3 + 3 + 3 + 3 + 3 + 9 = 24.$$

Because the sum of the average ranks of blanks meet the criterion of less than or equal to 26, the certification is acceptable.

Table E-3. Rank Sum Test, Example 3

<u>Standard Sample</u>	<u>Results</u>	<u>Rank</u>	<u>Average Rank</u>
Blank	NN	1	3
Blank	NN	2	3
Blank	NN	3	3
Blank	NN	4	3
Spike	NN	5	3
Spike	PP	6	7
Spike	PP	7	7
Spike	PP	8	7

NN = Negative; PP = Positive

$$\text{Average Rank for Negative Results} = \frac{1 + 2 + 3 + 4 + 5}{5} = 3$$

$$\text{Average Rank for Positive Results} = \frac{6 + 7 + 8}{3} = 7$$

$$\text{Sum of Average Ranks for Blanks} = 3 + 3 + 3 + 3 = 12.$$

Because the sum of the average ranks of blanks exceed the criterion of less than or equal to 10, the results are unacceptable, therefore,



Test an additional two blanks and two spikes:

<u>Standard Sample</u>	<u>Results</u>	<u>Rank</u>	<u>Average Rank</u> ***
Blank	NN	1	3.5
Blank	NN	2	3.5
Blank	NN	3	3.5
Blank	NN	4	3.5
Spike	NN	5	3.5
Blank-New	NN	6	3.5
Blank-New	PP	7	9.5
Spike	PP	8	9.5
Spike	PP	9	9.5
Spike	PP	10	9.5
Spike-New	PP	11	9.5
Spike-New	PP	12	9.5

$$*** \text{ Average Rank for Negative Results} = \frac{1 + 2 + 3 + 4 + 5 + 6}{6} = 3.5$$

$$\text{Average Rank for Positive Results} = \frac{7 + 8 + 9 + 10 + 11 + 12}{6} = 9.5$$

$$\text{Sum of Average Ranks for Blanks} = 3.5 + 3.5 + 3.5 + 3.5 + 3.5 + 9.5 = 27.$$

Because the sum of the average ranks of blanks exceed the criterion of less than or equal to 26, the certification is unacceptable. The target concentration must be increased or a different method must be used.



APPENDIX F

SAMPLE CONTAINER CLEANING PROCEDURES





APPENDIX F

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.



January 1990

USATHAMA PAM 11-41

Revision No. 0

APPENDIX G

STANDING OPERATING PROCEDURES FIELD OPERATIONS





APPENDIX G

STANDING OPERATING PROCEDURES FIELD OPERATIONS

The organization shall have written Standing Operating Procedures (SOPs) for all procedures and methods. SOPs shall be available for the following areas and shall contain, at a minimum, the information described.

- Training -- These SOPs describe the training procedures used to ensure that field personnel are qualified to perform the required functions.
- Sample Management -- These SOPs describe the numbering and labeling system, chain-of-custody procedures, and tracking of samples from collection to shipment or relinquishment to the laboratory. Sample management also includes the specification of holding times, volume of sample required by the laboratory, preservatives, and shipping requirements.
- Numbering and Labeling -- These SOPs describe the system for numbering and labeling samples. The numbering system shall ensure that a sample from a given location is assigned a unique number, and typically involves codes that explain information about the sample, such as matrix type, location, depth, and well number. The labeling SOPs shall specify the types of labels and markers to be used, typically waterproof, and the information to be included on the label, such as sample number, date and time of collection, sampler's name, matrix type, and type of analysis required.
- Sample Tracking -- These SOPs describe the procedures used to ensure that sample integrity is maintained from sampling and shipping through receipt in the laboratory. Chain-of-custody will be maintained and, therefore, possession shall be traceable from the time the samples are collected, through analysis, and finally to disposal. Typical information recorded on the custody form includes project name, signature of sampler(s), sampling station number, date and time of collection, and grab or composite sample designation. The signature of the individual(s) involved in sample transfer (i.e., relinquishing and accepting samples) must be documented.
- Sample Containers -- SOPs shall detail the specifications, including type and size of container and lid, for each container used in a sample collection activity. In addition, SOPs shall specify cleaning procedures to be followed prior to the use of the container to ensure that the container does not contaminate the sample. SOPs may also specify protocols for verifying the cleanliness of the containers through chemical analysis.
- Sample Preservation and Storage -- Preservation techniques are generally limited to pH control, chemical addition, refrigeration, and freezing. SOPs shall describe which preservation techniques apply to a method, how preservatives are added, the amount added, procedures



associated with shipping the preservative to the site, and any special handling or safety requirements.

- Holding Times -- Many analyses have a maximum time between collection and initiation of analytical work specified by either the method or regulations. If this time is exceeded, the analytes of interest may degrade and the data may be unusable. SOPs shall list holding times, if applicable, by method and sample matrix, and describe procedures for communicating holding time requirements to field personnel so that samples can be shipped to the laboratory in a timely manner.

- Shipping -- If the laboratory and sampling site are not in close proximity, the samples must be shipped. SOPs shall specify packaging procedures that prevent spills, maintain the required temperature, and meet Department of Transportation (DOT) requirements for shipping environmental or potentially hazardous samples. Instructions shall be provided for completing shipping papers. If holding times are crucial, SOPs should specify delivery to the laboratory within 24 hours or on weekends.

- Decontamination -- These SOPs describe the procedures used to clean field equipment before and during the sample collection process. The SOPs should include cleaning materials used, the order of washing and rinsing with the cleaning materials, requirements for protecting or covering cleaned equipment, procedures for disposing of cleaning materials, and safety considerations.

- Sample Collection Procedures -- SOPs for sample collection procedures shall describe how the procedures are actually performed in the field and not be a simple reference to standard methods, unless a procedure is performed exactly as described in the published method. The SOP for sample collection procedures should include the following:

- Applicability of the procedure;
- Equipment required;
- Detailed description of procedures to be followed in collecting the samples;
- Common problems encountered;
- Precautions to be taken; and
- Health and safety considerations.

It should include a statement that every effort shall be made to collect samples during the work week with samples delivered to the laboratory that same week.

- Corrective Action -- These SOPs describe procedures used to identify and correct deficiencies in the sample collection process. These should include specific steps to take in correcting deficiencies such as performing additional decontamination of equipment, resampling, and additional training of field personnel in methods procedures. The SOP shall specify that each corrective action must be documented with a description of the deficiency, the corrective action taken, and the person(s) responsible for implementing the corrective action.



- Records Management -- These SOPs describe the procedures for generating, controlling, and archiving field records. The SOPs should describe the responsibilities for record generation and control and the policies for record retention, including type, time, security, and retrieval and disposal authorities. Records shall include:

Project-specific records related to fieldwork performed for a group of samples. Project records may include correspondence, chain-of-custody, field notes, all reports issued as a result of the work, training records, project planning documents, and procedural SOPs used.

Field operations records, which document overall field operations. These records may include equipment performance and maintenance logs, personnel files, general field SOPs, and corrective action reports.

- Chemical and Sample Disposal -- These SOPs describe the policies and procedures for disposal of neat chemicals and standard and reagent solutions used in calibration of field equipment and decontamination procedures. Disposal of all chemicals must conform to federal, state, and local regulations.

- Reporting -- These SOPs describe the process for reporting the results of field activities.

In addition, where analyses are performed in the field, the following additional SOPs are required:

- Reagent/Standard Preparation -- These SOPs describe the procedures used to prepare and document every standard and reagent solution used in field operations. Information concerning specific grades of materials used in the preparation, appropriate glassware, containers for preparation, storage, labeling, recordkeeping for stocks and dilutions, and safety precautions to be taken should be included.

- Equipment Calibration and Maintenance -- These SOPs describe procedures used to ensure that field equipment and instrumentation are in working order. The SOPs describe calibration procedures and schedules, maintenance procedures and schedules, maintenance logs, service contractors or service arrangements for all equipment, and spare parts available in-house. Calibration and maintenance of field equipment and instrumentation shall be in accordance with manufacturers' specifications and shall be documented.

- Field Analysis -- All in situ, portable analysis, mobile labs, or other methods used in the field to determine a chemical or physical parameter shall be described by one or more SOPs. The SOPs shall incorporate applicable criteria from Appendix J.

- Data Reduction and Validation -- These SOPs describe procedures used to compute results from field measurements and to review and validate these data. They should include all formulas used to calculate results and procedures used to verify independently that field measurement results are correct.





APPENDIX H

SAMPLE PRESERVATION PROCEDURES AND HOLDING TIMES FOR AQUEOUS AND SOLID SAMPLES





APPENDIX H

SAMPLE PRESERVATION PROCEDURES AND HOLDING TIMES
FOR AQUEOUS AND SOLID SAMPLES

After the samples have been taken, they should be sent to the laboratory for analysis as expeditiously as possible in order to insure that the most reliable and accurate answers will be obtained as a result of the analysis. As a general rule, storage at low temperature is the best way to preserve most samples, although the length of time the sample can be held even at low temperatures varies with the analyte and matrix. The bottles should be packaged for shipping in insulated containers, constructed to insure that the bottles will arrive at the laboratory intact.

The following table summarizes containers, preservation, and holding time requirements by analyte and sample matrix. Regulations may supersede these listed requirements on occasion.

The time lapse between sample acquisition and analysis may not exceed the times shown in the table. Freezing samples to extend holding shall not be permitted.

As a result of a Holding Time Study performed by Oak Ridge National Laboratory, the following holding times are acceptable:

<u>PARAMETER</u>	<u>PRESERVATIVE</u>	<u>MAXIMUM HOLDING TIME FOR ALL MATRICES</u>
Volatile Organics	Sodium Bisulfate	28 days
Explosives	Cool, 4°C	56 days until extraction 40 days after extraction

NOTE: Contractual specifications may require analysis of samples within shorter time frames.



Table H-1. Containers, Preservation, Storage, and Holding Times^a

Table H-1. Containers, Preservation, Storage, and Holding Times ^a					
Parameter	Container ^b		Preservative ^{c,d}		Maximum Holding Time for all Matrices ^e
	Water	Soil	Water	Soil	
INORGANIC TESTS					
Acidity	P	G	Cool, 4°C	Cool, 4°C	14 days
Alkalinity	P	G	Cool, 4°C	Cool, 4°C	14 days
Ammonia	P	G	Cool, 4°C H ₂ SO ₄ to pH <2	Cool, 4°C	28 days
Asbestos	P	G	Cool, 4°C	Cool, 4°C	48 hours ^f
Bicarbonate	P	G	None Required	None Required	Analyze Immediately
Biochemical Oxygen Demand (BOD) and Carbonaceous BOD	P	G	Cool, 4°C	Cool, 4°C	48 hours
Bromide	P	G	None Required	None Required	28 days
Carbonate	P	G	None Required	None Required	Analyze Immediately
Chemical Oxygen Demand (COD)	P	G	Cool, 4°C H ₂ SO ₄ to pH <2	Cool, 4°C	28 days
Chloride	P	G	None Required	None Required	28 days
Chlorine, Total Residual	P	N/A	None Required	N/A	Analyze Immediately
Color	P	N/A	Cool, 4°C	N/A	48 hours



Table H-1. (Cont'd.)

Parameter	Container ^b		Preservative ^{c,d}		Maximum Holding Time for all Matrices ^e
	Water	Soil	Water	Soil	
Cyanide, Total and Amenable to Chlorination	P	G	Cool, 4°C NaOH to pH >12 0.6 g Ascorbic Acid/g	Cool, 4°C	14 days ^h
Dissolved Oxygen					
Probe	G Bottle and Top	N/A	None Required	N/A	Analyze Immediately
Winkler	G Bottle and Top	N/A	Fix On Site Store in Dark	N/A	8 hours
Fluoride	P	G	None Required	None Required	28 days
Hardness	P	N/A	HNO ₃ or H ₂ SO ₄ to pH<2	N/A	6 months
Hydrazine	P	G	If not analyzed immediately, collect under acid. Add 90 ml of sample to 10 ml HCl.	Cool, 4°C	7 days
Iodide	P	G	Cool, 4°C	Cool, 4°C	24 hours
Iodine	P	G	None Required	None Required	Analyze Immediately
Kjeldahl and Organic Nitrogen	P	G	Cool, 4°C H ₂ SO ₄ to pH <2	Cool, 4°C	28 days



Table H-1. (Cont'd.)

Parameter	Container ^b		Preservative ^{c,d}		Maximum Holding Time for all Matrices ^e
	Water	Soil	Water	Soil	
Metals ⁱ					
Chromium VI	P	G	Cool, 4°C	Cool, 4°C	24 hours
Mercury	P	G	HNO ₃ to pH <2	Cool, 4°C	28 days
Others	P	G	HNO ₃ to pH <2	Cool, 4°C	6 months
Nitrate	P	G	Cool, 4°C	Cool, 4°C	48 hours
Nitrate plus Nitrite	P	G	Cool, 4°C H ₂ SO ₄ to pH <2	Cool, 4°C	28 days
Nitrite	P	G	Cool, 4°C	Cool, 4°C	48 hours
Oil and Grease	G	G	Cool, 4°C H ₂ SO ₄ to pH <2	Cool, 4°C	28 days
Orthophosphate	P	G	Filter Immediately Cool, 4°C	Cool, 4°C	48 hours
pH	P	G	None Required	None Required	Analyze Immediately
Phenols	G	G	Cool, 4°C H ₂ SO ₄ to pH <2	Cool, 4°C	28 days
Phosphorous, Elemental	G	G	Cool, 4°C	Cool, 4°C	48 hours
Phosphorous, Total	P,G	G	Cool, 4°C H ₂ SO ₄ to pH <2	Cool, 4°C	28 days
Silica, Dissolved or Total	P	G	Cool, 4°C	Cool, 4°C	28 days



Table H-1. (Cont'd.)

Parameter	Container ^b		Preservative ^{c,d}		Maximum Holding Time for all Matrices ^e
	Water	Soil	Water	Soil	
Residue					
Filterable	P	N/A	Cool, 4°C	N/A	7 days
Settleable	P	N/A	Cool, 4°C	N/A	48 hours
Nonfilterable (TSS)	P	N/A	Cool, 4°C	N/A	7 days
Total	P	N/A	Cool, 4°C	N/A	7 days
Volatile	P	N/A	Cool, 4°C	N/A	7 days
Specific Conductance	P	G	Cool, 4°C	Cool, 4°C	28 days
Sulfate	P	G	Cool, 4°C	Cool, 4°C	28 days
Sulfide	P	G	Cool, 4°C Add Zinc Acetate plus NaOH to pH > 9	Cool, 4°C	7 days
Sulfite	P	G	None Required	None Required	Analyze Immediately
Surfactants	P	G	Cool, 4°C	Cool, 4°C	48 hours
Temperature	P	G	None Required	None Required	Analyze Immediately
Turbidity	P	N/A	Cool, 4°C	N/A	48 hours
<u>ORGANIC TESTS^j</u>					
Acrolein and Acrylonitrile	S	S	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ^g Adjust pH to 4-5 ^k	Cool, 4°C	14 days ^k

Table H-1. (Cont'd.)

Parameter	Container ^b		Preservative ^{c,d}		Maximum Holding Time for all Matrices ^e
	Water	Soil	Water	Soil	
Benzidines ¹	G	G	Cool, 4°C ^m 0.008% Na ₂ S ₂ O ₃ ^g pH 2-7	Cool, 4°C	7 days until extraction ⁿ
Chlorinated Hydrocarbons ¹	G	G	Cool, 4°C	Cool, 4°C	7 days until extraction 40 days after extraction
Haloethers ¹	G	G	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ^g	Cool, 4°C	7 days until extraction 40 days after extraction
Nitroaromatics and Isophorone	G	G	Cool, 4°C Store in Dark	Cool, 4°C Store in Dark	7 days until extraction 40 days after extraction
Nitrosamines ^{1,o}	G	G	Cool, 4°C Store in Dark 0.008% Na ₂ S ₂ O ₃ ^g	Cool, 4°C Store in Dark	7 days until extraction 40 days after extraction
PCBs	G	G	Cool, 4°C	Cool, 4°C	7 days until extraction 40 days after extraction
Pesticides ¹	G	G	Cool, 4°C pH 5-9 ^p	Cool, 4°C	7 days until extraction 40 days after extraction
Phenols ¹	G	G	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ^g	Cool, 4°C	7 days until extraction 40 days after extraction
Phthalate Esters ¹	G	G	Cool, 4°C	Cool, 4°C	7 days until extraction 40 days after extraction



Table H-1. (Cont'd.)

Parameter	Container ^b		Preservative ^{c,d}		Maximum Holding Time for all Matrices ^e
	Water	Soil	Water	Soil	
Polynuclear Aromatic Hydrocarbons	G	G	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ^g Store in Dark	Cool, 4°C Store in Dark	7 days until extraction 40 days after extraction
Purgeable Aromatic Hydrocarbons	S	S	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ^g HCl to pH < 2 ^q	Cool, 4°C	14 days ^q
Purgeable Halocarbons	S	S	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ^g	Cool, 4°C	14 days
TCDD ¹	G	G	Cool, 4°C 0.008% Na ₂ S ₂ O ₃ ^g	Cool, 4°C	7 days until extraction 40 days after extraction
Total Organic Carbon	G	G	Cool, 4°C HCl or H ₂ SO ₄ to pH < 2	Cool, 4°C	28 days
Total Organic Halogen	G	G	Cool, 4°C 1 ml of 0.1 M sodium sulfite	Cool, 4°C	7 days

Analytes not listed should be preserved at 4°C and held not longer than 7 days.

^aPreservatives and holding times are from Federal Register, Vol. 49, No. 209, Friday, October 26, 1984, Page 43260 and Characterization of Hazardous Waste Sites: A Methods Manual -- Volume II, Sampling Methods, Second Edition, EPA-600/4-84-076. Container requirements are consistent with these references.

^bp = Polyethylene

G = Amber Glass with Teflon-lined cap

S = Glass Vial with Teflon-lined septum cap



c Sample preservation should be performed immediately upon sample collection. For composite samples, each aliquot should be preserved at the time of collection. When use of an automatic sampler makes it impossible to preserve each aliquot, samples may be preserved by maintaining at 4°C until compositing and sample splitting is completed.

d When any sample is to be shipped by common carrier or sent through the U.S. Mail, it must comply with the Department of Transportation Hazardous Materials Regulations (49 CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance. For the preservation requirements in this table, the Office of Hazardous Materials, Materials Transportation Bureau, Department of Transportation, has determined that the Hazardous Materials Regulations do not apply to the following materials: Hydrochloric acid (HCl) in water solutions at concentrations of 0.04% by weight or less (pH about 1.96 or greater); Nitric acid (HNO₃) in water solutions at concentrations of 0.15% by weight or less (pH about 1.62 or greater); Sulfuric acid (H₂SO₄) in water solutions at concentrations of 0.35% by weight or less (pH about 1.15 or greater); and Sodium hydroxide (NaOH) in water solutions at concentrations of 0.080% by weight or less (pH about 12.3 or less).

e Samples should be analyzed as soon as possible after collection. The times listed are the maximum times that samples may be held before analysis and still be considered valid.

A laboratory is obligated to hold the sample for a shorter time if knowledge exists to show this is necessary to maintain sample integrity.

f If samples cannot be filtered within 48 hours, add 1 ml of a 2.71% solution of mercuric chloride to inhibit bacterial growth.

g Should only be used in the presence of residual chlorine.

h Maximum holding time is 24 hours when sulfide is present. Optionally, all samples may be tested with lead acetate paper before pH adjustment in order to determine if sulfide is present. If sulfide is present, it can be removed by addition of cadmium nitrate powder until a negative spot test is obtained. The sample is filtered and then NaOH is added to pH 12.

i For dissolved metals, filter immediately on site before adding preservative.



^jGuidance applies to samples to be analyzed by GC, LC, or GC/MS for specific compounds.

^kThe pH adjustment is not required if acrolein will not be measured. Samples for acrolein receiving no pH adjustment must be analyzed within three days of sampling.

^lWhen the extractable analytes of concern fall within a single chemical category, the specified preservative and maximum holding times must be observed for optimum safeguard of sample integrity. When the analytes of concern fall within two or more chemical categories, the sample may be preserved by cooling to 4°C, reducing residual chlorine with 0.008% sodium thiosulfate, storing in the dark, and adjusting pH to 6-9; samples preserved in this manner may be held for 7 days before extraction and 40 days after extraction. Exceptions to this optimal preservation and holding time procedure are noted in footnotes g, m, and n.

^mIf 1,2-diphenylhydrazine is likely to be present, adjust the pH of the sample to 4.0 ± 0.2 to prevent rearrangement to benzidine.

ⁿExtracts may be stored up to 7 days before analysis if storage is conducted under an inert (oxidant-free) atmosphere.

^oFor the analysis of diphenylnitrosamine, add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$ and adjust pH to 7-10 with NaOH within 24 hours of sampling.

^pThe pH adjustment may be performed upon receipt at the laboratory and may be omitted if the samples are extracted within 72 hours of collection. For the analysis of aldrin, add 0.008% $\text{Na}_2\text{S}_2\text{O}_3$.

^qSample receiving no pH adjustment must be analyzed within 7 days of sampling.





January 1990

USATHAMA PAM 11-41

Revision No. 0

APPENDIX I

SARM REPOSITORY PROGRAM





APPENDIX I

SARM REPOSITORY PROGRAM

I.1 SARM DEVELOPMENT

Due to the limited availability of reference materials for trace organic analyses from the NIST, USATHAMA has initiated a program for the development of standard analytical reference materials (SARMs) for use in its programs.

Candidate methods for high purity analyses are selected and evaluated on a preliminary basis, using known materials. Appropriate standards (traceable to NIST) are selected and procured. Sufficient analyses are run to document the random and systematic errors in the analyses. The most appropriate method of high purity analysis is selected for the evaluation of the analytical standards.

Raw materials are synthesized or procured and purified to greater than 98 mole percent. Purities above 98 mole percent can be conveniently and precisely determined in many cases by differential scanning calorimetry using the premelting technique. Wet analyses are used where required. Precision and accuracy data must be presented to support each high purity analysis used to guarantee a standard. Chromatographic analyses are used only to estimate impurities and thus, support an analysis by difference. Chromatographic, spectrophotometric, and NMR examination are routinely used to ensure that each material of certified high purity is indeed the correct compound.

Each SARM is subjected to an aggravated storage period to estimate its stability. Materials showing a propensity for decomposition are repurified and stabilized if practical. If repurification and stabilization are not practical, an alternate standard must be selected. SARMs should emerge from aggravated storage with purities in excess of 98 mole percent. Any standard obtained from any other source than USATHAMA are not considered to be SARMs.

I.1.1. CRITERIA FOR TEST RESULTS

Results of the aggravated storage tests are expressed as mole percent purity before and after the two week test. Unanticipated observations concerning the condition of the standard are noted. Test conditions are fully documented. If the purity of the standard does not fall below the 98 mole percent value and there are no conditions observed in the standard that would interfere with the analytical system, the standard passes the test.



I.1.2. TEST PROCEDURE

Liquid SARMs are sealed in glass bottles with crimp-type septum tops or glass ampules, while solid SARMs are sealed in screw top bottles. The SARMs are sealed under normal atmosphere and stored at 70°C for 2 weeks. These SARMs are then cooled and stored in a freezer until they can be analyzed. If a standard degrades below 98 mole percent, the cause is sought and special storage conditions are developed. Special storage conditions might include dark glass containers, inert atmosphere, lowered temperature, or addition of a stabilizer. If a material is found to be too unstable for storage, a new SARM is selected. The analytical technique initially used to guarantee the purity of each new SARM is repeated after aggravated storage in order to detect degradation.

I.1.3. REPORTS

The results of aggravated storage tests are submitted to the USATHAMA Chemistry Branch. The Chemistry Branch reviews the suitability of each material and all its supporting data for adequacy as a SARM.

I.2. SARM SURVEILLANCE PROGRAM

At six-month intervals, surveillance samples are removed from the repository and reanalyzed by the original acceptance methods.

I.2.1. PURPOSE

The purpose of this surveillance program is to confirm the integrity of each SARM by scheduled analyses.

I.2.2. CONDITIONS

All SARMs are protected from UV radiation and stored in bulk at 0°C. SARMs which have been purchased in 98 mole percent purity are stored in the manufacturer's container. Where possible, purified SARMs are stored in glass stoppered flasks which have been sealed with Parafilm. Glass bottles with crimp-tops are used where necessary (e.g., DIMP "creeps" around glass stoppers so it would be sealed in crimp-top bottles). Air sensitive compounds are stored



under inert atmosphere. Hygroscopic compounds are stored with desiccant in a sealed outer container.

I.2.3. TEST PROCEDURE

A specimen is withdrawn (under the appropriate atmosphere) from each SARM at prescribed intervals. Purities of these specimens are determined using the original acceptance methods.

I.2.4. CRITERIA FOR SURVEILLANCE

The standards must remain at least 98 mole percent pure through the surveillance program. If a SARM fails to meet this criterion, its use is suspended immediately and all laboratories using it are notified by the central repository by phone.

I.2.5. PROGRAM

The surveillance program for each SARM begins when the material is purified and placed in the 0°C repository. If further purification is indicated by the aggravated storage phase, the surveillance period is reinitiated upon completion of the repurification. Thus, the aggravated storage is carried out concomitantly with the first 2 weeks of the first surveillance cycle. Any required subsequent repurification of the SARM reinitiates the surveillance program. Each surveillance cycle lasts 6 months. The entire program continues for 2 years for each SARM. After 2 years, aggravated storage will be repeated on a specimen of the original materials or newly obtained material as availability and projected needs for the material at that time dictate. Materials which have been deleted from the surveys will be removed from the surveillance program at the convenience of USATHAMA.

I.3. USER REPORTING

The user laboratory shall report any problems with received SARMS or observed degradation of any SARM immediately to the USATHAMA Chemistry Branch.





January 1990

USATHAMA PAM 11-41

Revision No. 0

APPENDIX J

STANDING OPERATING PROCEDURES LABORATORY OPERATIONS





APPENDIX J

STANDING OPERATING PROCEDURES LABORATORY OPERATIONS

The laboratory shall have written standing operating procedures (SOPs) for all procedures and methods. SOPs shall be available for the following areas and shall contain, at a minimum, the information described:

- Training-- These SOPs describe the training procedures used by the laboratory to ensure that personnel are qualified to perform the required analyses.
- Sample Receipt and Logging -- These SOPs describe the precautions to be used in opening sample shipment containers, as well as procedures used to verify that chain-of-custody has been maintained, to examine samples for damage, to check for proper preservatives and temperature, to assign the testing program, and to log samples into the laboratory sample streams.
- Sample and Extract Storage -- These SOPs describe the storage conditions for all samples, procedures used to verify and document daily storage temperature, and procedures used to ensure that custody of the samples is maintained while in the laboratory.
- Sample Scheduling -- These SOPs describe the procedures and criteria used for scheduling work in the laboratory, including procedures used to ensure that holding times or contract analytical/reporting requirements, if applicable, are met.
- Preventing Sample Contamination -- These SOPs describe the procedures that will be used to prevent cross contamination or lab contamination of samples and extracts.
- Security for Laboratory and Samples -- These SOPs describe the procedures for ensuring that equipment or samples in the laboratory are not tampered with and the limit of access to authorized personnel only.
- Traceability/Equivalency of Standards -- These SOPs describe the procedures for the obtaining of standards and their inventory and the methods to be employed for the characterization of non-SARMs and the demonstration of equivalency for secondary standards.



- Standard Solution Verification -- These SOPs detail the procedures used to prepare, verify, and document every standard and reagent solution, including reagent-grade water, used in the laboratory. Information concerning specific grades of materials used in the preparation, appropriate glassware and containers for preparation and storage, labeling and recordkeeping for stocks and dilutions, procedures used to verify concentration and purity, and safety precautions to be taken should be included in the SOPs.
- Maintaining Instrument Records and Logbooks -- These SOPs describe procedures used to ensure that laboratory equipment and instrumentation are in working order. The SOPs describe calibration procedures and schedules, maintenance procedures and schedules, maintenance logs, service contracts or service arrangements for all equipment, and spare parts available in-house. Calibration and maintenance of laboratory equipment and instrumentation shall be in accordance with manufacturers' specifications and shall be documented.
- Sample Analysis and Data Control Systems -- These SOPs describe procedures that are used for the operation of the sample analysis and data control systems.
- Glassware Cleaning -- These SOPs describe the procedures that are used in the cleaning of glassware used in the laboratory.
- Technical and Managerial Review of Laboratory Operations and Data Package Preparation -- These SOPs describe the procedures that are used to ensure that operations are being carried out according to requirements, in a timely manner and the interaction between management and the laboratory staff.
- Internal Review and Contractually Required Quality Assurance and Quality Control Data for Each Individual Data Package -- These SOPs detail the type, purpose, and frequency of QC samples analyzed in the laboratory. They should include information on the applicability of the QC sample to the analytical process, the statistical treatment of the data, and the responsibility of laboratory staff and management in generating and using the data.
- Sample Analysis, Data Handling and Reporting -- SOPs for analytical methods shall be a description of how the analysis is actually performed in the laboratory. These SOPs should include the following:



- Sample preparation and analysis procedures including applicable holding time, extraction, digestion, or preparation steps as appropriate to the method; procedures for determining the appropriate dilution to analyze; and any other information required to perform the analysis accurately and consistently.
- Instrument standardization, including concentration and frequency of analysis of calibration standards, linear range of the method, and calibration acceptance criteria.
- Raw data recording requirements and documentation including sample identification number, analyst, data verification analyst, date of analysis and verification, and computational method(s).
- Data Reduction and Validation -- These SOPs describe the procedures used to compute analytical results from data and to review and validate the data. They should include all formulas used to calculate the results, procedures for computing and interpreting the results from QC samples, and procedures used to independently verify that the analytical results are correct. In addition, routine procedures used to monitor precision and accuracy, including evaluations of reagent, field, and trip blanks, calibration standards, control samples, duplicate and matrix spike samples, and surrogate recovery should be detailed in an SOP. The validation of data entry into the IRDMS shall be included, i.e., check of transfer file versus input data.
- Chain-of-Custody -- These SOPs describe the procedures to be followed for controlling internal chain of custody of samples and extracts, and reporting problems of chain-of-custody from sampling contractor.
- Document Control, Including Data Package Preparation -- These SOPs describe the procedures being used to control all the data output from the analysis. They conclude the procedures for the preparation of the data package and its subsequent review.
- Corrective Action -- These SOPs describe procedures used to identify and correct deficiencies in the analytical process. These include specific steps to take in correcting deficiencies such as preparation of new standards and reagents, recalibration and restandardization of equipment, reanalysis of samples, and additional training of laboratory personnel in methods and procedures. The SOP shall specify that each corrective action must be documented with a description of the deficiency, the corrective action taken, and the person(s) responsible for implementing the corrective action.
- Records Management -- These SOPs describe the procedures for generating, controlling, and archiving laboratory records. The SOPs should detail the responsibilities for record generation and control; policies for record retention; including type, time, security, and retrieval and disposal authorities. Records shall include:



- Project-specific records related to analyses performed for a group of samples. Project records may include an index of documents, correspondence, chain-of-custody records, request for analysis, calibration records, raw and finished analytical and QC data, data reports, and project planning documents.

- Laboratory operations records, which document the overall laboratory operation. These records may include laboratory notebooks, instrument performance and maintenance logs, software documentation, control charts, reference material certification, personnel files, laboratory SOPs, and corrective action reports.



January 1990

USATHAMA PAM 11-41

Revision No. 0

APPENDIX K

OUTLIER TEST





APPENDIX K

OUTLIER TEST

An extreme observation (outlier) is a datum that appears to be different from the main data pattern. Such observations may be caused by the following:

- A measurement that was read, recorded, or transcribed incorrectly;
- A faulty instrument;
- Incorrectly prepared standards;
- Incorrect calculations;
- Incorrect application of an analytical method;
- Degradation of standard or spiking solutions;
- Environmental conditions that have changed significantly; or
- Other unidentified instrumental problems.

The principal safeguards against obtaining or using an outlier are vigilance during all operations and visual inspection of data before performing statistical analyses.

If a datum falls above or below the control limits of either the $\bar{X}$ or R control chart or if identified as an outlier by Dixon's test, the value shall be investigated. Sometimes the investigation will reveal a recording or computational mistake that can be revised to obtain the correct value. If an error is found but the correct value cannot be determined, the erroneous value shall not be used in statistical calculations. When errors are found, either correctable or uncorrectable, all analytical results for that lot must be inspected to ensure that erroneous results are not reported. If an uncorrectable error affected results of environmental samples, the lot shall be judged as out-of-control and analyses must be repeated.



K.1 DIXON'S TEST

Dixon's test expresses the gap between an outlier and the nearest value as a fraction of the range between the smallest and largest value.

The entire data set must be ordered from highest to lowest, with the highest value assigned a rank of 1 (X_1) and the lowest value a rank of n (X_n). The test criterion (r) varies with sample size, as follows:

- For less than eight measurements, reject X_n (the lowest value) if

$$\frac{X_n - X_{(n-1)}}{X_n - X_1} > r(10);$$

- For less than eight measurements, reject X_1 (the highest value) if

$$\frac{X_2 - X_1}{X_n - X_1} > r(10);$$

- Between eight and ten measurements, reject X_n (the lowest value) if

$$\frac{X_n - X_{(n-1)}}{X_n - X_2} > r(11);$$

- Between eight and ten measurements, reject X_1 (the highest value) if

$$\frac{X_2 - X_1}{X_{(n-1)} - X_1} > r(11);$$

- Between eleven and thirteen measurements, reject X_n (the lowest value) if

$$\frac{X_n - X_{(n-2)}}{X_n - X_2} > r(21);$$

- Between eleven and thirteen measurements, reject x_1 (the highest value) if

$$\frac{X_3 - X_1}{X_{(n-1)} - X_1} > r(21);$$

- Over thirteen measurements, reject X_n (the lowest value) if

$$\frac{X_n - X_{(n-2)}}{X_n - X_3} > r(22);$$



- Over thirteen measurements, reject X_1 (the highest value) if

$$\frac{X_3 - X_1}{X_{(n-2)} - X} > r(22).$$

The critical values for the test statistic at 98 percent confidence level are shown in Table K-1. If the test statistic is greater than the critical value from the Table, then the data point is an outlier. Once adequate data are available, n shall be kept constant at 20, with the 20 most recent data points being used.



Table K-1. CRITICAL VALUES FOR DIXON'S OUTLIER TEST

Number of Measurements (n)	Criterion (r)	Critical Value of r (a = 0.02)	Critical Value of r (a = 0.05)
3	r_{10}	0.976	0.941
4		0.846	0.765
5		0.729	0.642
6		0.644	0.560
7		0.586	0.507
8	r_{11}	0.631	0.554
9		0.587	0.512
10		0.551	0.477
11	r_{21}	0.638	0.576
12		0.605	0.546
13		0.578	0.521
14	r_{22}	0.602	0.546
15		0.579	0.525
16		0.559	0.507
17		0.542	0.490
18		0.527	0.475
19		0.514	0.462
20		0.502	0.450
21		0.491	0.440
22		0.481	0.430
23		0.472	0.421
24		0.464	0.413
25		0.457	0.406



APPENDIX L

$\bar{x}$ - R CHART DATA TABULATION AND GRAPHING
FOR DUPLICATE SPIKE RECOVERY



SINGLE DAY XBAR REPORT FOR PERCENT RECOVERY

 | Laboratory:TH | Date:11/13/89 |

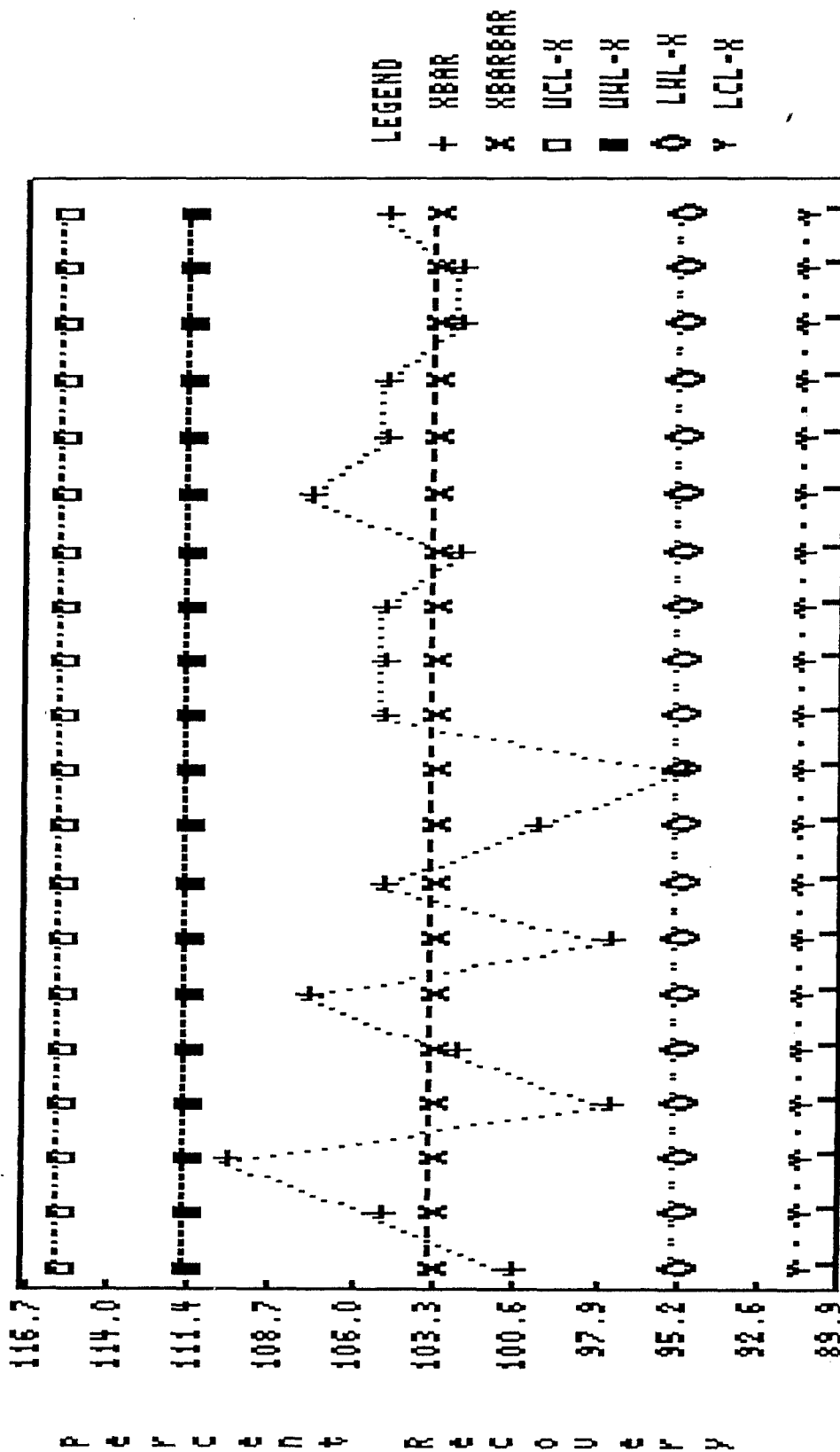
 | Method:XD07 | Test Name:BA |

Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	XBAR	UCLX	UWLX	LWLX	LCLX
043087	CF2	2.00	2	2.05	2	1.98	2	102.5	99.0	100.7	107.3	105.1	96.3	94.1
043087	CF4	2.00	2	2.10	2	2.10	2	105.0	105.0	105.0	106.0	104.9	100.7	99.6
050187	ACE	2.00	2	2.20	2	2.20	2	110.0	110.0	110.0	107.5	106.7	103.7	102.9
050287	ACP	2.00	2	1.80	2	2.10	2	90.0	105.0	97.5	111.9	109.0	97.5	94.7
050387	ACZ	2.00	2	2.10	2	2.00	2	105.0	100.0	102.5	111.9	109.0	97.2	94.3
050587	ADJ	2.00	2	2.20	2	2.10	2	110.0	105.0	107.5	112.7	109.8	98.0	95.1
050787	ADT	2.00	2	2.10	2	1.80	2	105.0	90.0	97.5	114.7	110.7	95.2	91.3
050987	AED	2.00	2	2.00	2	2.20	2	100.0	110.0	105.0	115.8	111.6	94.8	90.6
051187	AEN	2.00	2	1.80	2	2.20	2	90.0	110.0	100.0	118.3	113.1	92.6	87.5
051387	AEX	2.00	2	1.80	2	2.00	2	90.0	100.0	95.0	117.7	112.5	91.7	86.5
051587	AFI	2.00	2	2.20	2	2.00	2	110.0	100.0	105.0	118.3	112.9	91.7	86.3
051787	AFS	2.00	2	2.10	2	2.10	2	105.0	105.0	105.0	117.3	112.3	92.8	87.9
051987	AGC	2.00	2	2.10	2	2.10	2	105.0	105.0	105.0	116.2	111.7	93.7	89.2
052187	AGM	2.00	2	2.05	2	2.05	2	102.5	102.5	102.5	115.3	111.1	94.3	90.1
052387	AGW	2.00	2	2.10	2	2.20	2	105.0	110.0	107.5	115.4	111.2	94.7	90.6
052587	AHG	2.00	2	2.10	2	2.10	2	105.0	105.0	105.0	114.9	110.9	95.4	91.5
052787	AHQ	2.00	2	2.20	2	2.00	2	110.0	100.0	105.0	115.3	111.3	95.3	91.3
060387	AIA	2.00	2	2.20	2	1.90	2	110.0	95.0	102.5	116.2	111.8	94.6	90.2
061087	AIL	2.00	2	2.10	2	2.00	2	105.0	100.0	102.5	116.0	111.7	94.7	90.4



Single Day X-BAR Control Chart - HIGH Spike Concentration

Laboratory TH Test BA Method XDB7



FROM 04/30/87 TO 06/20/87



SINGLE DAY XBAR REPORT FOR PERCENT RECOVERY

 | Laboratory:TH | Date:11/13/89 |

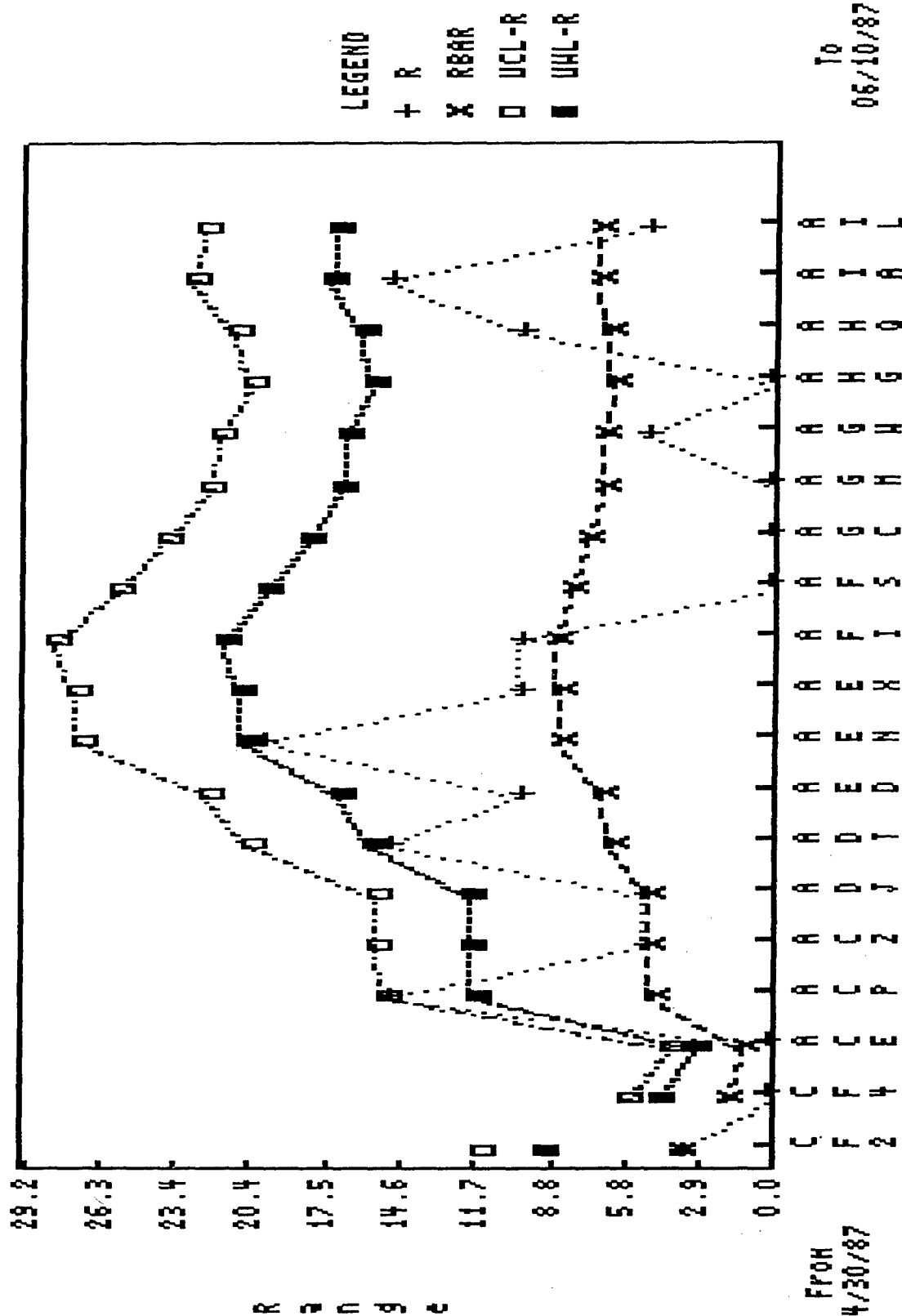
 | Method:XD07 | Test Name:BA |

Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	XBAR	UCLX	UWLX	LWLX	LCLX
043087	CF2	2.00	2	2.05	2	1.98	2	102.5	99.0	100.7	115.5	111.4	95.2	91.1
043087	CF4	2.00	2	2.10	2	2.10	2	105.0	105.0	105.0	115.5	111.4	95.2	91.1
050187	ACE	2.00	2	2.20	2	2.20	2	110.0	110.0	110.0	115.5	111.4	95.2	91.1
050287	ACP	2.00	2	1.80	2	2.10	2	90.0	105.0	97.5	115.5	111.4	95.2	91.1
050387	ACZ	2.00	2	2.10	2	2.00	2	105.0	100.0	102.5	115.5	111.4	95.2	91.1
050587	ADJ	2.00	2	2.20	2	2.10	2	110.0	105.0	107.5	115.5	111.4	95.2	91.1
050787	ADT	2.00	2	2.10	2	1.80	2	105.0	90.0	97.5	115.5	111.4	95.2	91.1
050987	AED	2.00	2	2.00	2	2.20	2	100.0	110.0	105.0	115.5	111.4	95.2	91.1
051187	AEN	2.00	2	1.80	2	2.20	2	90.0	110.0	100.0	115.5	111.4	95.2	91.1
051387	AEX	2.00	2	1.80	2	2.00	2	90.0	100.0	95.0	115.5	111.4	95.2	91.1
051587	AFI	2.00	2	2.20	2	2.00	2	110.0	100.0	105.0	115.5	111.4	95.2	91.1
051787	AFS	2.00	2	2.10	2	2.10	2	105.0	105.0	105.0	115.5	111.4	95.2	91.1
051987	AGC	2.00	2	2.10	2	2.10	2	105.0	105.0	105.0	115.5	111.4	95.2	91.1
052187	AGM	2.00	2	2.05	2	2.05	2	102.5	102.5	102.5	115.5	111.4	95.2	91.1
052387	AGW	2.00	2	2.10	2	2.20	2	105.0	110.0	107.5	115.5	111.4	95.2	91.1
052587	AHG	2.00	2	2.10	2	2.10	2	105.0	105.0	105.0	115.5	111.4	95.2	91.1
052787	AHQ	2.00	2	2.20	2	2.00	2	110.0	100.0	105.0	115.5	111.4	95.2	91.1
060387	AIA	2.00	2	2.20	2	1.90	2	110.0	95.0	102.5	115.5	111.4	95.2	91.1
061087	AIL	2.00	2	2.10	2	2.00	2	105.0	100.0	102.5	115.5	111.4	95.2	91.1
062087	AJX	1.50	2	1.57	2	1.58	2	104.7	105.3	105.0	115.5	111.4	95.2	91.1



Single Day Range Control Chart - HIGH Spike Concentration

Laboratory TH Test BA Method XD07



SINGLE DAY R REPORT FOR PERCENT RECOVERY

 | Laboratory:TH | Date:11/13/89 |

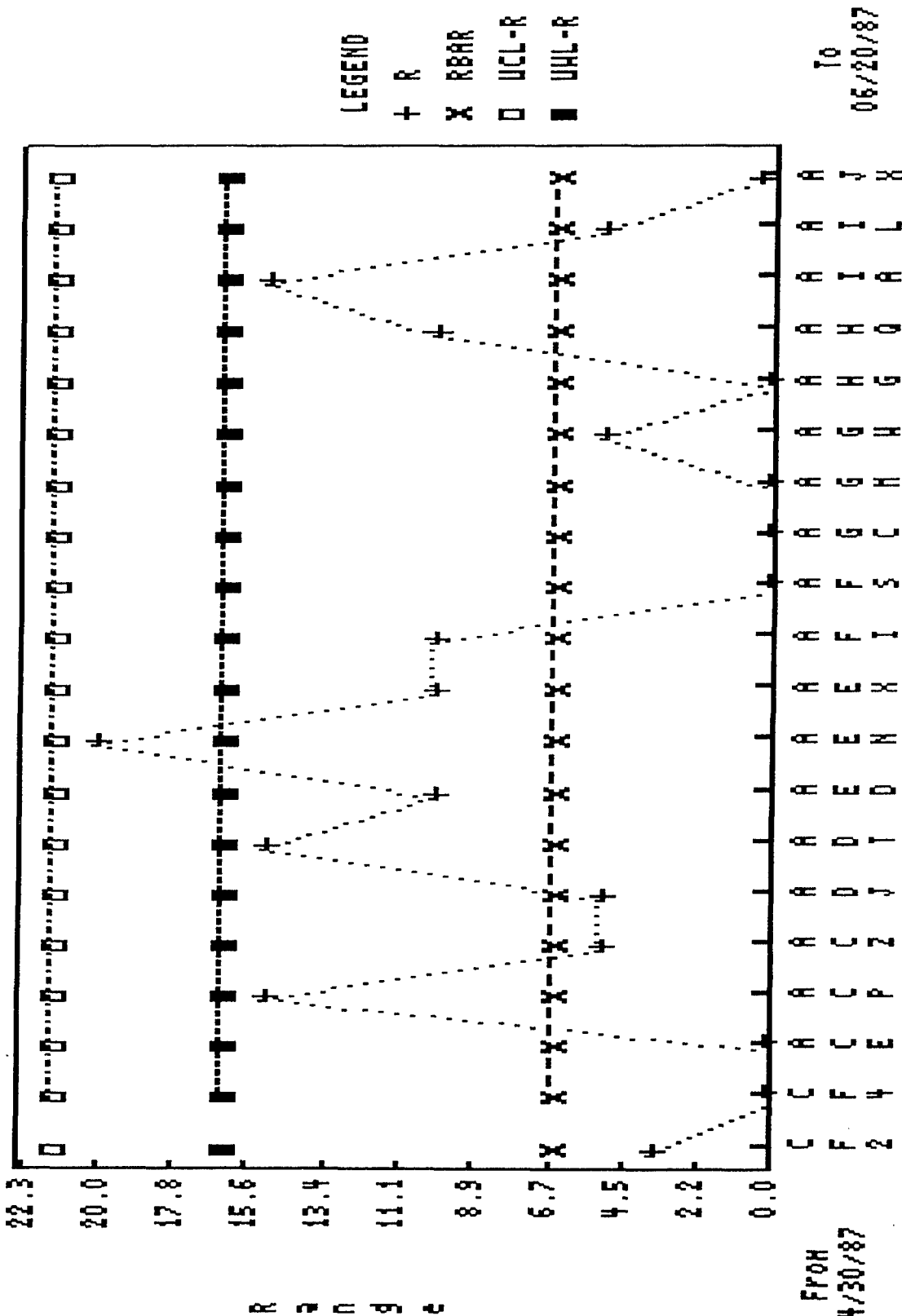
 | Method:XD07 | Test Name:BA |

Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	R	UCLR	UWLR	Outlie
r													
-----	----	-----	----	-----	----	-----	----	-----	-----	-----	-----	-----	-----
043087	CF2	2.00	2	2.05	2	1.98	2	102.5	99.0	3.5	11.4	8.8	.F.
043087	CF4	2.00	2	2.10	2	2.10	2	105.0	105.0	0.0	5.6	4.3	.F.
050187	ACE	2.00	2	2.20	2	2.20	2	110.0	110.0	0.0	3.9	3.0	.F.
050287	ACP	2.00	2	1.80	2	2.10	2	90.0	105.0	15.0	15.0	11.6	.F.
050387	ACZ	2.00	2	2.10	2	2.00	2	105.0	100.0	5.0	15.4	11.8	.F.
050587	ADJ	2.00	2	2.20	2	2.10	2	110.0	105.0	5.0	15.4	11.8	.F.
050787	ADT	2.00	2	2.10	2	1.80	2	105.0	90.0	15.0	20.3	15.6	.F.
050987	AED	2.00	2	2.00	2	2.20	2	100.0	110.0	10.0	21.9	16.8	.F.
051187	AEN	2.00	2	1.80	2	2.20	2	90.0	110.0	20.0	26.8	20.6	.F.
051387	AEX	2.00	2	1.80	2	2.00	2	90.0	100.0	10.0	27.1	20.8	.F.
051587	AFI	2.00	2	2.20	2	2.00	2	110.0	100.0	10.0	27.8	21.3	.F.
051787	AFS	2.00	2	2.10	2	2.10	2	105.0	105.0	0.0	25.5	19.6	.F.
051987	AGC	2.00	2	2.10	2	2.10	2	105.0	105.0	0.0	23.5	18.1	.F.
052187	AGM	2.00	2	2.05	2	2.05	2	102.5	102.5	0.0	21.9	16.8	.F.
052387	AGW	2.00	2	2.10	2	2.20	2	105.0	110.0	5.0	21.6	16.6	.F.
052587	AHG	2.00	2	2.10	2	2.10	2	105.0	105.0	0.0	20.3	15.6	.F.
052787	AHQ	2.00	2	2.20	2	2.00	2	110.0	100.0	10.0	20.9	16.1	.F.
060387	AIA	2.00	2	2.20	2	1.90	2	110.0	95.0	15.0	22.5	17.3	.F.
061087	AIL	2.00	2	2.10	2	2.00	2	105.0	100.0	5.0	22.2	17.1	.F.



Single Day Range Control Chart - HIGH Spike Concentration

Laboratory TH Test BA Method XD07



SINGLE DAY R REPORT FOR PERCENT RECOVERY

 | Laboratory:TH | Date:11/13/89 |

 | Method:XD07| Test Name:BA |

Date	Lot	QC Man	QC Exp	X1 Man	X1 Exp	X2 Man	X2 Exp	%X1	%X2	R	UCLR	UWLR	Outlie r
-----	---	----	----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
043087	CF2	2.00	2	2.05	2	1.98	2	102.5	99.0	3.5	21.2	16.3	.F.
043087	CF4	2.00	2	2.10	2	2.10	2	105.0	105.0	0.0	21.2	16.3	.F.
050187	ACE	2.00	2	2.20	2	2.20	2	110.0	110.0	0.0	21.2	16.3	.F.
050287	ACP	2.00	2	1.80	2	2.10	2	90.0	105.0	15.0	21.2	16.3	.F.
050387	ACZ	2.00	2	2.10	2	2.00	2	105.0	100.0	5.0	21.2	16.3	.F.
050587	ADJ	2.00	2	2.20	2	2.10	2	110.0	105.0	5.0	21.2	16.3	.F.
050787	ADT	2.00	2	2.10	2	1.80	2	105.0	90.0	15.0	21.2	16.3	.F.
050987	AED	2.00	2	2.00	2	2.20	2	100.0	110.0	10.0	21.2	16.3	.F.
051187	AEN	2.00	2	1.80	2	2.20	2	90.0	110.0	20.0	21.2	16.3	.F.
051387	AEX	2.00	2	1.80	2	2.00	2	90.0	100.0	10.0	21.2	16.3	.F.
051587	AFI	2.00	2	2.20	2	2.00	2	110.0	100.0	10.0	21.2	16.3	.F.
051787	AFS	2.00	2	2.10	2	2.10	2	105.0	105.0	0.0	21.2	16.3	.F.
051987	AGC	2.00	2	2.10	2	2.10	2	105.0	105.0	0.0	21.2	16.3	.F.
052187	AGM	2.00	2	2.05	2	2.05	2	102.5	102.5	0.0	21.2	16.3	.F.
052387	AGW	2.00	2	2.10	2	2.20	2	105.0	110.0	5.0	21.2	16.3	.F.
052587	AHG	2.00	2	2.10	2	2.10	2	105.0	105.0	0.0	21.2	16.3	.F.
052787	AHQ	2.00	2	2.20	2	2.00	2	110.0	100.0	10.0	21.2	16.3	.F.
060387	AIA	2.00	2	2.20	2	1.90	2	110.0	95.0	15.0	21.2	16.3	.F.
061087	AIL	2.00	2	2.10	2	2.00	2	105.0	100.0	5.0	21.2	16.3	.F.
062087	AJX	1.50	2	1.57	2	1.58	2	104.7	105.3	0.6	21.2	16.3	.F.





APPENDIX M

$\bar{x}$ - R CHART DATA TABULATION AND GRAPHING FOR
THREE-POINT MOVING AVERAGE SPIKE RECOVERY



THREE DAY MOVING AVERAGE XBAR REPORT FOR PERCENT RECOVERY

 | Laboratory:TH | Date:11/13/89 |
 | Method:XD07 | Test Name:BA |

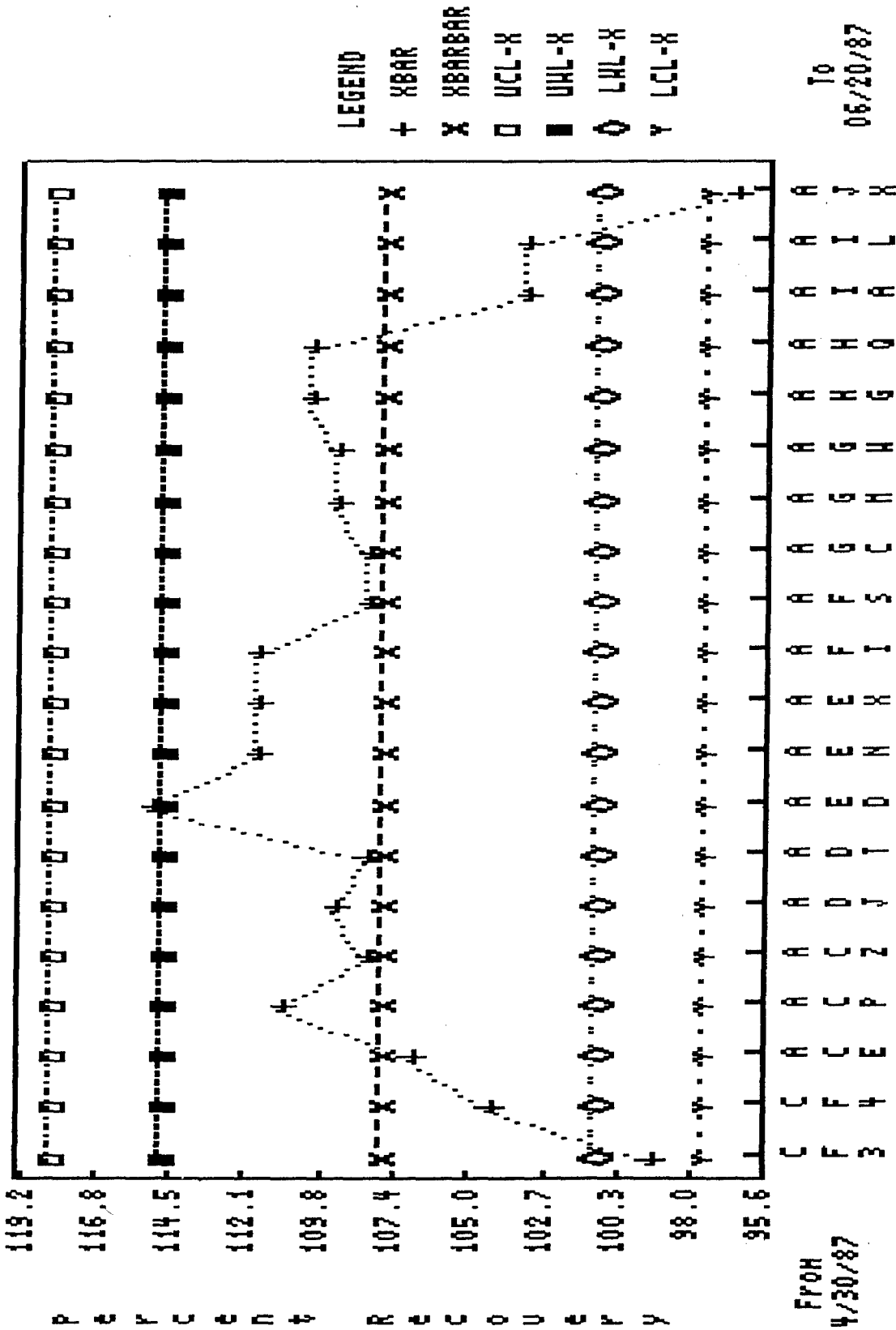
Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX
-----	---	----	----	----	----	-----	-----	-----	-----	-----	-----
043087	CF1	4.00	1	3.90	1	97.5	0.0	0.0	0.0	0.0	0.0
043087	CF2	4.00	1	3.50	1	87.5	0.0	0.0	0.0	0.0	0.0
043087	CF3	4.00	1	4.50	1	112.5	99.2	124.8	116.2	82.1	73.6
043087	CF4	4.00	1	4.50	1	112.5	104.2	127.3	118.7	84.6	76.1
050187	ACE	4.00	1	3.80	1	95.0	106.7	126.4	118.7	88.1	80.4
050287	ACP	4.00	1	4.30	1	107.5	110.8	123.7	117.5	92.9	86.7
050387	ACZ	4.00	1	4.00	1	100.0	108.3	123.2	117.4	94.2	88.4
050587	ADJ	4.00	1	4.10	1	102.5	109.2	122.6	117.2	95.6	90.2
050787	ADT	4.00	1	4.00	1	100.0	108.3	122.5	117.2	96.2	90.9
050987	AED	4.00	1	4.80	1	120.0	115.0	122.4	117.5	97.9	93.0
051187	AEN	4.00	1	4.40	1	110.0	111.7	121.6	117.1	99.3	94.8
051387	AEX	4.00	1	4.40	1	110.0	111.7	120.8	116.7	100.3	96.2
051587	AFI	4.00	1	4.40	1	110.0	111.7	120.2	116.4	101.2	97.4
051787	AFS	4.00	1	4.00	1	100.0	108.3	120.3	116.4	101.2	97.3
051987	AGC	4.00	1	4.00	1	100.0	108.3	120.3	116.4	101.0	97.1
052187	AGM	4.00	1	4.10	1	102.5	109.2	120.3	116.4	101.2	97.3
052387	AGW	4.00	1	4.10	1	102.5	109.2	120.3	116.4	101.2	97.3
052587	AHG	4.00	1	4.20	1	105.0	110.0	120.1	116.3	101.5	97.7
052787	AHQ	4.00	1	4.20	1	105.0	110.0	119.8	116.2	101.6	98.0
060387	AIA	4.00	1	4.00	1	100.0	103.3	119.2	115.7	101.5	98.0
061087	AIL	4.00	1	4.00	1	100.0	103.3	118.6	115.2	101.4	98.0



January 1990

Three Day X-BAR Control Chart - LOW Spike Concentration

Laboratory TH Test BA Method XD87



THREE DAY MOVING AVERAGE XBAR REPORT FOR PERCENT RECOVERY

 | Laboratory:TH | Date:11/13/89 |
 | Method:XD07 | Test Name:BA |

Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	XBAR	UCLX	UWLX	LWLX	LCLX
-----	----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
043087	CF1	4.00	1	3.90	1	97.5	0.0	118.1	114.7	100.9	97.5
043087	CF2	4.00	1	3.50	1	87.5	0.0	118.1	114.7	100.9	97.5
043087	CF3	4.00	1	4.50	1	112.5	99.2	118.1	114.7	100.9	97.5
043087	CF4	4.00	1	4.50	1	112.5	104.2	118.1	114.7	100.9	97.5
050187	ACE	4.00	1	3.80	1	95.0	106.7	118.1	114.7	100.9	97.5
050287	ACP	4.00	1	4.30	1	107.5	110.8	118.1	114.7	100.9	97.5
050387	ACZ	4.00	1	4.00	1	100.0	108.3	118.1	114.7	100.9	97.5
050587	ADJ	4.00	1	4.10	1	102.5	109.2	118.1	114.7	100.9	97.5
050787	ADT	4.00	1	4.00	1	100.0	108.3	118.1	114.7	100.9	97.5
050987	AED	4.00	1	4.80	1	120.0	115.0	118.1	114.7	100.9	97.5
051187	AEN	4.00	1	4.40	1	110.0	111.7	118.1	114.7	100.9	97.5
051387	AEX	4.00	1	4.40	1	110.0	111.7	118.1	114.7	100.9	97.5
051587	AFI	4.00	1	4.40	1	110.0	111.7	118.1	114.7	100.9	97.5
051787	AFS	4.00	1	4.00	1	100.0	108.3	118.1	114.7	100.9	97.5
051987	AGC	4.00	1	4.00	1	100.0	108.3	118.1	114.7	100.9	97.5
052187	AGM	4.00	1	4.10	1	102.5	109.2	118.1	114.7	100.9	97.5
052387	AGW	4.00	1	4.10	1	102.5	109.2	118.1	114.7	100.9	97.5
052587	AHG	4.00	1	4.20	1	105.0	110.0	118.1	114.7	100.9	97.5
052787	AHQ	4.00	1	4.20	1	105.0	110.0	118.1	114.7	100.9	97.5
060387	AIA	4.00	1	4.00	1	100.0	103.3	118.1	114.7	100.9	97.5
061087	AIL	4.00	1	4.00	1	100.0	103.3	118.1	114.7	100.9	97.5
062087	AJX	4.00	1	3.60	1	90.0	96.7	118.1	114.7	100.9	97.5

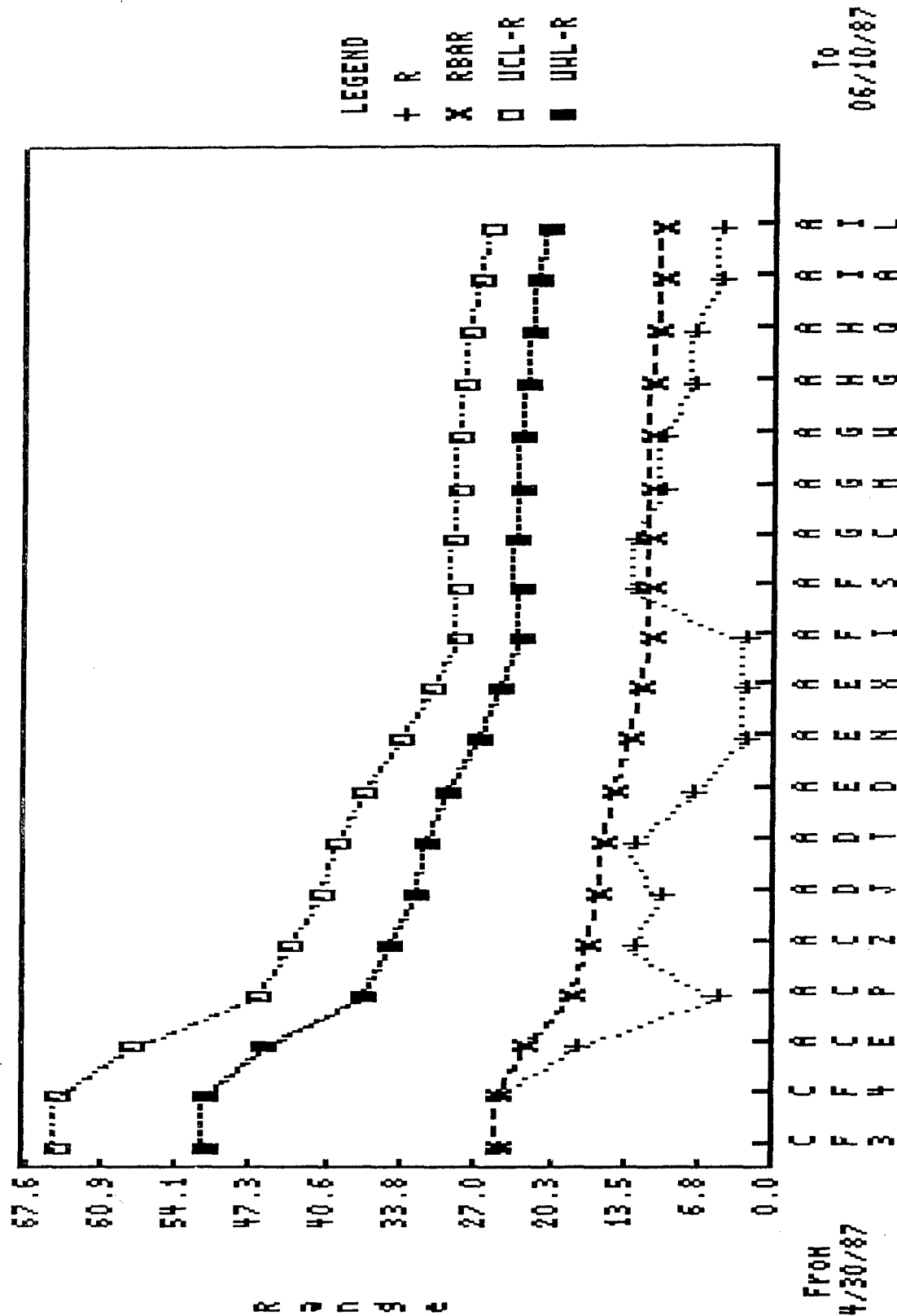


Three Day Range Control Chart - LOW Spike Concentration

Method XD07

Test BA

Laboratory TH



THREE DAY MOVING AVERAGE R REPORT FOR PERCENT RECOVERY

 | Laboratory:TH | Date:11/13/89 |

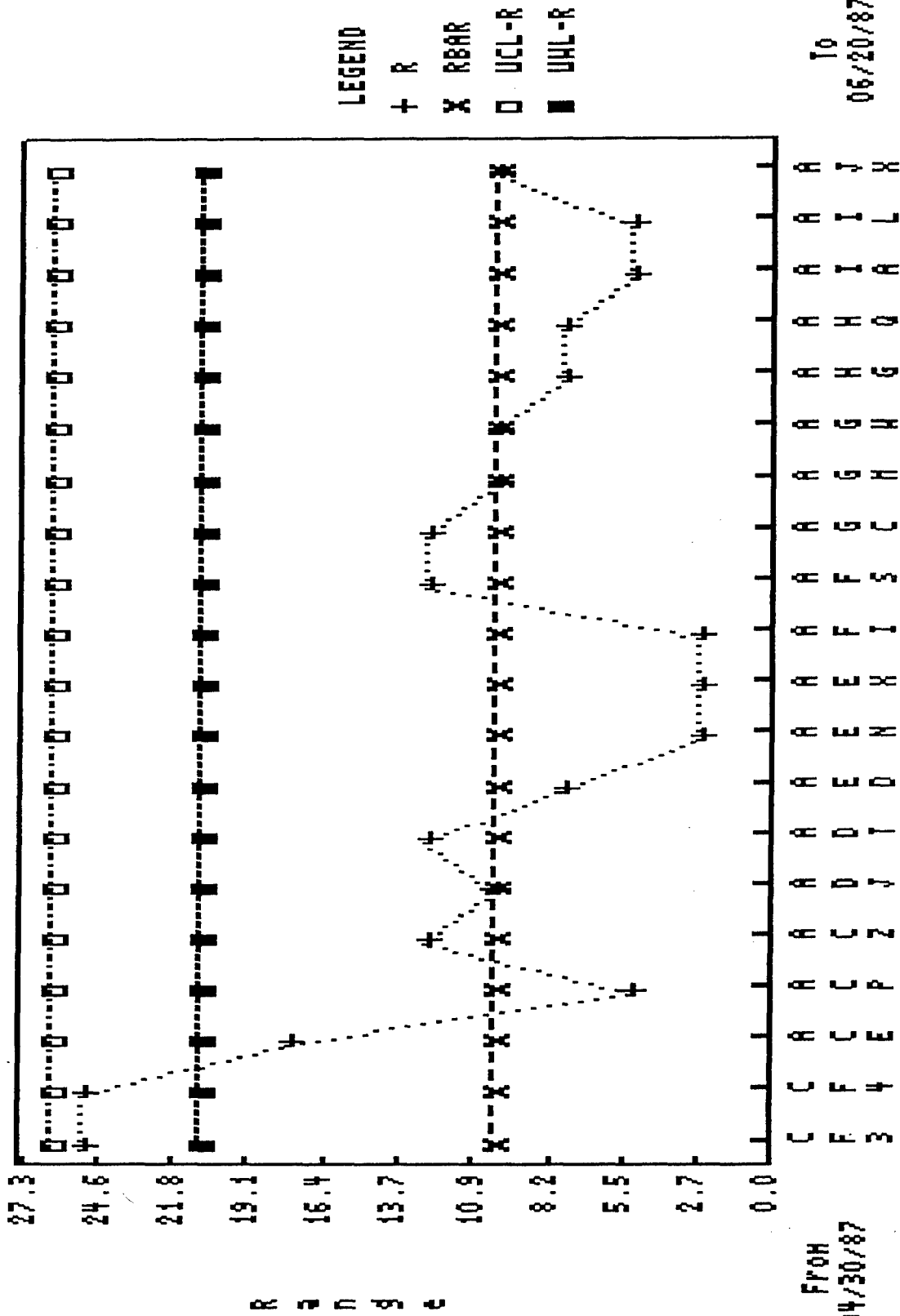
 | Method:XD07| Test Name:BA |

Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR	Outlier
043087	CF1	4.00	1	3.90	1	97.5	0.0	0.0	0.0	.F.
043087	CF2	4.00	1	3.50	1	87.5	0.0	0.0	0.0	.F.
043087	CF3	4.00	1	4.50	1	112.5	25.0	64.4	51.2	.F.
043087	CF4	4.00	1	4.50	1	112.5	25.0	64.4	51.2	.F.
050187	ACE	4.00	1	3.80	1	95.0	17.5	57.9	46.1	.F.
050287	ACP	4.00	1	4.30	1	107.5	5.0	46.6	37.1	.F.
050387	ACZ	4.00	1	4.00	1	100.0	12.5	43.8	34.8	.F.
050587	ADJ	4.00	1	4.10	1	102.5	10.0	40.7	32.4	.F.
050787	ADT	4.00	1	4.00	1	100.0	12.5	39.7	31.6	.F.
050987	AED	4.00	1	4.80	1	120.0	7.5	37.1	29.5	.F.
051187	AEN	4.00	1	4.40	1	110.0	2.5	33.7	26.9	.F.
051387	AEX	4.00	1	4.40	1	110.0	2.5	30.9	24.6	.F.
051587	AFI	4.00	1	4.40	1	110.0	2.5	28.6	22.8	.F.
051787	AFS	4.00	1	4.00	1	100.0	12.5	28.8	23.0	.F.
051987	AGC	4.00	1	4.00	1	100.0	12.5	29.1	23.2	.F.
052187	AGM	4.00	1	4.10	1	102.5	10.0	28.8	23.0	.F.
052387	AGW	4.00	1	4.10	1	102.5	10.0	28.8	23.0	.F.
052587	AHG	4.00	1	4.20	1	105.0	7.5	28.1	22.3	.F.
052787	AHQ	4.00	1	4.20	1	105.0	7.5	27.6	21.9	.F.
060387	AIA	4.00	1	4.00	1	100.0	5.0	26.8	21.3	.F.
061087	AIL	4.00	1	4.00	1	100.0	5.0	26.0	20.7	.F.



Three Day Range Control Chart - LOW Spike Concentration

Laboratory TH Test BA Method XD07



THREE DAY MOVING AVERAGE R REPORT FOR PERCENT RECOVERY

 | Laboratory:TH | Date:11/13/89 |

 | Method:XD07| Test Name:BA |

Date	Lot	QC Man	QC Exp	X Man	X Exp	%X	R	UCLR	UWLR	Outlier
043087	CF1	4.00	1	3.90	1	97.5	0.0	26.0	20.7	.F.
043087	CF2	4.00	1	3.50	1	87.5	0.0	26.0	20.7	.F.
043087	CF3	4.00	1	4.50	1	112.5	25.0	26.0	20.7	.F.
043087	CF4	4.00	1	4.50	1	112.5	25.0	26.0	20.7	.F.
050187	ACE	4.00	1	3.80	1	95.0	17.5	26.0	20.7	.F.
050287	ACP	4.00	1	4.30	1	107.5	5.0	26.0	20.7	.F.
050387	ACZ	4.00	1	4.00	1	100.0	12.5	26.0	20.7	.F.
050587	ADJ	4.00	1	4.10	1	102.5	10.0	26.0	20.7	.F.
050787	ADT	4.00	1	4.00	1	100.0	12.5	26.0	20.7	.F.
050987	AED	4.00	1	4.80	1	120.0	7.5	26.0	20.7	.F.
051187	AEN	4.00	1	4.40	1	110.0	2.5	26.0	20.7	.F.
051387	AEX	4.00	1	4.40	1	110.0	2.5	26.0	20.7	.F.
051587	AFI	4.00	1	4.40	1	110.0	2.5	26.0	20.7	.F.
051787	AFS	4.00	1	4.00	1	100.0	12.5	26.0	20.7	.F.
051987	AGC	4.00	1	4.00	1	100.0	12.5	26.0	20.7	.F.
052187	AGM	4.00	1	4.10	1	102.5	10.0	26.0	20.7	.F.
052387	AGW	4.00	1	4.10	1	102.5	10.0	26.0	20.7	.F.
052587	AHG	4.00	1	4.20	1	105.0	7.5	26.0	20.7	.F.
052787	AHQ	4.00	1	4.20	1	105.0	7.5	26.0	20.7	.F.
060387	AIA	4.00	1	4.00	1	100.0	5.0	26.0	20.7	.F.
061087	AIL	4.00	1	4.00	1	100.0	5.0	26.0	20.7	.F.
062087	AJX	4.00	1	3.60	1	90.0	10.0	26.0	20.7	.F.





January 1990

USATHAMA PAM 11-41

Revision No. 0

APPENDIX N

SPIKING SOLUTION CONTROL





APPENDIX N

SPIKING SOLUTION CONTROL

STATEMENT OF PROBLEM:

Analysis of spiked standard soil and laboratory reagent water forms the basis of control for all analytical methods in the USATHAMA program. These spiked control samples utilize stock solutions which are made and maintained separately from stock solutions prepared for instrument calibration.

Occasionally, when recovery of spiked analyte for control samples is poor, the question arises as to the integrity of these spiking solutions. In the past, no routine testing procedure has been required by USATHAMA although some laboratories have instituted programs of their own.

Thus, often in the past, historical data has not been available to resolve whether problems in analyte recovery were due to the integrity of spiking solutions or some other cause. Generally when these questions have arisen, new spiking solutions have been prepared and if the problem went away with the next spiked lot, the blame was fixed on the integrity of the old spiking solutions.

TWO PROBLEMS ARE ASSOCIATED WITH THIS PROCEDURE:

1. Coincident removal of the problem when new spiking solutions are prepared is not conclusive evidence that the old spiking solution was the problem.
2. Whether the solution had deteriorated or not, there is then no basis to make judgements on the status of that lot of analysis or other lots spiked before the problem with the spiking solution was detected. Thus, this retrospective approach often leaves USATHAMA in the position of having to decide whether or not to accept analytical data for lots where no control data is available. What is needed is a positive approach which keeps control on spiking solutions before usage.

REQUIRED SOLUTION:

Dilute working spike solutions will be validated against working standards before initial use and within seven days before subsequent usage. The method of validation should utilize the same technology used for measurement in environmental samples. GC/FID may be substituted for GC/MS with approval from the USATHAMA Chemistry Branch.



For single analyte solutions and the multiple analyte solutions used for other than GC/MS procedures, recovery must be greater than the lower warning limit on the $\bar{x}$ control chart for that analyte. If the same solution is used to spike water and soil, the control chart that exhibits the more stringent control limit will be used. If a solution is suspected of deterioration at other times, it will be tested before it is discarded to assess its status and allow judgements on spiked control samples prepared since the last solution validation.

For the multiple analyte surrogate spiking solutions for GC/MS, recovery of all surrogates must be greater than the lower control limits on the $\bar{X}$ control chart if GC/MS is used for validation. If GC/FID is used, the recovery must be greater than the lower warning limit.

The required approach described above will require additional work for some laboratories although this procedure may informally already be in place. It will provide the QA staff at each laboratory, as well as USATHAMA, additional information to assess data quality.



January 1990

USATHAMA PAM 11-41

Revision No. 0

APPENDIX O

MODIFIED LIMITS





APPENDIX O

MODIFIED CONTROL LIMITS (MCL) FOR $\bar{x}$ CHARTSINTRODUCTION

The ultimate goal of control charts is to help produce results of consistent and defined quality. When methods are exceptionally precise and accurate, data quality may significantly exceed requirements for the planned and use of the results (Data Quality Objectives). For example, suppose the control mean ($\bar{x}$) is 99.5 percent with the Upper Control Limit (UCL) at 104.5 percent and the Lower Control Limit (LCL) at 94.5 percent. A lot mean of 106.0 percent would represent an out-of-control situation. However, random sampling uncertainties might suggest that recoveries between 85.0 percent and 115.0 percent would meet data quality objectives for the project. The indication of lack-of-control would not be ignored but the rejection of lot results would not be warranted.

Another important factor that applies to control charts based on duplicate spiked QC samples in each lot is that only within-day variations are reflected in the average range ($\bar{R}$) used to set upper and lower control limits on $\bar{x}$. Because lot-to-lot calibration variability is excluded from R , it has been found that 10-25 percent of lot QC means will fall slightly outside of normal control limits. These minor excursions usually don't represent a true out-of-control condition and remedial action is only required when two or more successive means are outside control limits unless, of course, a mean is highly divergent.

When the average recovery differs greatly from 100 percent, many lot QC means may fail to meet data quality specifications even though reproducibility keeps these means within control limits. Alternatively, average recovery could be good but with unacceptable reproducibility. Modified Control Limits in conjunction with normal control limits on $\bar{x}$ offer a means to deal with these situations.

PROCEDURE

All previously specified steps in customary control chart establishment are followed (Section 11.4). However, upper and lower warning limits are replaced by modified limits (UML $\bar{x}$ and LML $\bar{x}$) that are derived from upper and lower specification limits for individual recoveries (USL X and LSL X) using the following equations:

$$\text{UML on Average: } \text{UML } \bar{x} = \text{USL } X - M_3 \bar{R}$$

$$\text{LML on Average: } \text{LML } \bar{x} = \text{LSL } X + M_3 \bar{R}$$



Values for M_3 depend on the number of individual measurements in each lot mean ($\bar{x}$) and are designed to insure that each replicate measurement will be within the specification limits, except for genuine outliers. The upper and lower specification limits (USL X and LSL X) will be provided by the USATHAMA Chemistry Branch for those methods where a statistically valid data base has been established.

For duplicate spike QC samples (Section 11.4.1), the equations become:

$$\text{UML } \bar{x} = \text{USL X} - 0.78 \bar{R}$$

$$\text{LML } \bar{x} = \text{LSL X} + 0.78 \bar{R}$$

Modified limits can also be used with moving average control charts. In contrast to duplicate spiked QC samples in each lot, $\bar{R}$ for the three-lot moving average and moving range does include lot-to-lot variability. Therefore, a high percentage of out-of-control means should not occur for measurements in a state-of-control. However, modified limits are very useful in meeting data quality specifications. For procedures with measurement capability that is superior to requirements, acceptance of lot data are facilitated for a QC moving average that is outside of control limits but within modified limits. For procedures with performance that is inadequate to meet specifications due to large $\bar{R}$ or poor accuracy, moving averages outside of modified limits command attention to improving precision and accuracy even when the averages are within current control limits.

For moving averages of $n = 3$ (Section 11.4.2) the equations for modified limits are:

$$\text{UML } \bar{x} = \text{USL X} - 0.75 \bar{R}$$

$$\text{LML } \bar{x} = \text{LSL X} + 0.75 \bar{R}$$



APPENDIX P

PRECERTIFICATION/CERTIFICATION PERFORMANCE DATA PACKAGE CHECKLISTS





APPENDIX P

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 _____ in _____.
Analyte(s) 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



APPENDIX P

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 _____ in _____.
Analyte(s) 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.

- _____ 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





APPENDIX Q

CONTROL CHART CHECKLIST





APPENDIX Q

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



APPENDIX Q

INSTRUCTIONS FOR CONTROL CHART CHECKLIST

- Item 1. The USATHAMA method number(s) under which the control charts were generated that are included in this current package are to be listed in numerical order.
- Item 2. A summary table shall be prepared listing the method number(s), USATHAMA lots, dates of analysis, and analytes that are included in this package.
- Items 3 & 4. All $\bar{x}$ - R control charts generated in the control of analyses performed during this period shall be included. Each control chart shall include the following information:
- Analyte
 - Method number
 - Laboratory
 - Spike concentration
 - Chart title - one of the following:
 - Single Day $\bar{x}$ Control Chart
 - Single Day R Control Chart
 - Three-Point Moving Average $\bar{x}$ Control Chart
 - Three-Point Moving Average R Control Chart
 - Three-letter lot designation and analysis date for each point, shown on the x-axis
 - Percent Recovery (for $\bar{x}$ control charts) or Range (for R control charts) along the y-axis
 - Upper control limit (UCL), on $\bar{x}$ and R control charts
 - Upper warning limit (UWL), on $\bar{x}$ and R control charts



- Mean, on $\bar{x}$ and R control charts
- Lower warning limit (LWL), on $\bar{x}$ control charts
- Lower control limit (LCL), on $\bar{x}$ control charts.

The charts must contain sufficient data so that any trends, if present, could be discerned. (Charts developed during the initial stages of any analysis shall contain all points.

Charts developed after the process has been stabilized, at least 20 points, shall contain at a minimum the most recent 10 points). Any point(s) that exceed the control limits shall be flagged (by circling in red) for discussion under 5b below. Any outlier tests must be included.

- Item 5. The observations made during the review of the control charts, including but not limited to the items listed, shall be submitted in writing.
- Item 5a. A discussion of any trends observed, the possible start of any trend, or the lack thereof, shall be included. A trend can be defined as seven points on the same side of mean, five points going in one direction or a cyclical representation of data.
- Item 5b. An analysis of any points flagged on the control chart(s) as being out-of-control shall be included. Discussion should attempt to describe the cause of the out-of-control status and whether the point(s) are to be expected due to the random statistics used to demonstrate control or are the results of a possible systematic error or bias that would affect the analytical results. The discussion should include evaluation of outlier test results.
- Item 5c. Describe all actions taken to get process back into control.
- Item 5d. The data generated to prove that the analysis are back in control along with the criteria used ascertaining same shall be included.
- Item 6. Recommendations made as to the acceptance or rejection of the lot analysis, based on Item 5. above.





January 1990

USATHAMA PAM 11-41

Revision No. 0

APPENDIX R

CONTRACTOR QAC CHECKLIST



APPENDIX R

CONTRACTOR QAC CHECKLIST

Before releasing data for transmission to permanent storage, for use by other project participants, or for submission via the USATHAMA IRDMS, the Contractor QAC shall complete the attached checklist. One checklist shall be completed for each analytical lot. The QAC shall retain the checklist with the analytical data for the lot. The data, checklist file, and data package arranged by lot for each installation, may be inspected during any laboratory audit. The complete data/checklist file shall be forwarded to USATHAMA at the end of a project.



APPENDIX R
CONTRACTOR QAC CHECKLIST

Contract/Task Number _____ Installation _____

Method Number _____ Method _____

Analyte(s) _____ Lot Designation _____

<u>No</u> <u>Yes</u>		<u>QA Program</u> <u>Reference</u>	<u>Comments</u>
I. Holding Times			
☐ ☐	Extraction Time Met	6.8 and Appendix H	
☐ ☐	Analysis Time Met	6.8 and Appendix H	
II. Calibration			
A. Initial			
1. ☐ ☐	Initial Calibra- tion Performance	8.1.1 or 8.1.3	
2. ☐ ☐	LOF Test Performed	Appendix B	
3. ☐ ☐	Zero Intercept Test Performed	Appendix B	
4. ☐ ☐	Points Plotted	8.1.1	
B. Daily			
1. ☐ ☐	Daily Calibration Performed	8.1.2 or 8.1.4	
2. ☐ ☐	Daily Criteria Met	8.1.2 or 8.1.4	



<u>No</u>	<u>Yes</u>	<u>QA Program</u>	<u>Reference</u>	<u>Comments</u>
If II.B.2 is NO:				
—	—	Daily Standard Reanalyzed	8.1.2 or 8.1.4	
—	—	Daily Criteria Met	8.1.2 or 8.1.4	
—	—	Initial Calibra- tion Performed	8.1.1 or 8.1.3	
—	—	Initial Criteria Met	8.1.1 or 8.1.3	
3.	—	—	End of Day Cali- bration Performed	8.1.2 or 8.1.4
4.	—	—	End of Day Criteria Met	8.1.2 or 8.1.4

If II.B.4 is NO:

☐	☐ Standard Reanalyzed	8.1.2 or 8.1.4	
☐	☐ Criteria Met	8.1.2 or 8.1.4	
☐	☐ Sample Results Rejected	8.1.2 or 8.1.4	
☐	☐ Blow-up of manually Integrated peak(s) examined and commented on	10.5.1.2	

III. Quality Control

A.	☐ Blank and Correct Spikes in Sample Lot	11.2	



<u>No</u>	<u>Yes</u>		<u>QA Program Reference</u>	<u>Comments</u>
B.	☐	Data Plotted on Control Chart(s)	11.4	
C.	☐	Control Points Within Limits	11.4	

If III.C is NO:

1.	☐	Outlier Test Performed	Appendix K	
2.	☐	Acceptable Explana- tion Provided	11.5	
3.	☐	Corrective Actions Implemented and Documented	15.0	
4.	☐	Control Reestablished	11.5	
5.	☐	Lot Reanalyzed	11.5	

IV. Sample Analysis

A.	☐	Reported Concen- trations within Certified Range	10.4	

If IV.A is NO:

	☐	Extracts Diluted within Range	10.4.1 or 10.4.2	
B.	☐	All Results have Correct Signifi- cant Figures	10.4	

Contractor QAC

Date





APPENDIX S

SAMPLE RECEIPT CHECKLIST





APPENDIX S

SAMPLE RECEIPT CHECKLIST

	<u>Yes</u>	<u>No</u>	<u>Comment</u>
A. Sample Cooler			
1. Is evidence tape intact?			
2. Chain of Custody forms provided; filled out properly/completely?			
3. Blue ice (or equiv) included ____; temp recorded ____.			
4. Samples intact, i.e., bottles not broken, caps in place.			
B. Samples			
1. Bottles labelled.			
2. Labels agree with chain-of-custody form.			
3. Bottles correct for type of sample.			
4. Sample volume adequate for required tests.			
5. Preservatives added, where required.			
6. Evidence tape on bottles.			
C. Log in			
1. Site ID/field number entered in logbook.			
2. USATHAMA number assigned and entered.			
3. Label on bottle annotated with USATHAMA number.			





APPENDIX T

DATA PACKAGE CHECKLISTS





APPENDIX T

DATA PACKAGE CHECKLISTS

Each data package will have a series of checklists associated with it as an aid in the determination of its completeness and as a means of checking compliance with USATHAMA requirements. These checklists will include, but are not limited to:

- Data package checklist;
- Data package document inventory list;
- Data review checklist;
- Report checklist.

The final step in the review of a data package are the signing by the QAC of the checklist and the attesting to the fact that the data are correct and defensible.



APPENDIX T

DATA PACKAGE CHECKLISTLotMethod Number

I have checked this report and data package to make certain that the following conditions are in compliance with USATHAMA requirements:

I. GENERAL

- ☐ 1. All enclosed copies are legible and not excessively reduced.
- ☐ 2. There are no "yellow stickies," tablet sheets, or other undocumented forms in the data package.
- ☐ 3. All required documents, including a completed chain-of-custody form, are enclosed.
- ☐ 4. The data block on the outside of the data package are complete, with all other relevant information included.

II. NOTEBOOK PAGES

- ☐ 5. All copies of notebook pages are identified by notebook number and page number.
- ☐ 6. All units ("ug/L"; "ug/g"; "mL") are clearly defined.
- ☐ 7. Each page has been signed and dated by the analyst and reviewer.
- ☐ 8. All written explanations have all of the necessary information included and may stand alone as written.

III. COMPUTER DATA SHEET

- ☐ 9. The preliminary computer data sheet has been signed and dated by both the reviewer and the analyst.

IV. CHROMATOGRAMS AND STRIP CHARTS

- ☐ 10. All enclosed chromatograms and/or strip charts have been labelled properly, signed, and dated by the analyst.



V. CHECKLISTS

- ___ 11. All enclosed checklists are the current version, and have either each blank initialled or the blanks checked with a signature at the bottom of the page.

VII. CORRECTIONS

- ___ 12. No white-out or correction tape has been used on any raw data.
- ___ 13. All cross-outs consist of only a single line, and have been initialled and dated.
- ___ 14. All cross-outs have a legitimate, sufficient explanation alongside.

Analyst Signature Date

Checker Signature Date

Data were obtained while the analytical process was in-control and meet the agreed upon Data Quality Objectives.

QAC Signature

Date



APPENDIX T

DATA PACKAGE DOCUMENT INVENTORY LISTLotMethod Number

Analyst: If the listed document is in the data package, please initial inventory list.

- _____ Review sign-off sheet;
- _____ Chain-of-custody sheet, laboratory;
- _____ Chain-of-custody sheet, field;
- _____ Reagent blank report form;
- _____ Screening chromatogram - dated and initialed by analyst;
- _____ Unknown analyte report sheet;
- _____ Best fit spectra for each unknown peak;
- _____ NIST library search for unknowns;
- _____ Coding form or approved data reporting form;
- _____ Copy of extraction logbook pages;
- _____ Copy of sample preparation logbook pages;
- _____ Copy of analyst's notebook pages;
- _____ Copy of moisture logbook pages;
- _____ Copy of standards preparation (logbook pages);
- _____ Raw data output - dated and initialed by analyst (printouts, etc.);
- _____ DFTPP 12 hour tuning and mass calibration report(s);
- _____ BFB 12 hour tuning and mass calibration report(s);
- _____ Initial calibration data, including RIC, and quantitation reports for four standards;
- _____ Daily calibration data, including RIC, and quantitation report;
- _____ RIC and quantitation report for: field samples, QC samples, blank samples;
- _____ Check standard results;
- _____ Chromatogram or strip chart recorded output with analyte peak indicated, dated, and initialed by analyst;
- _____ Expanded scale blow-up of manually integrated peak;
- _____ Unknown report, library search, best fit spectra;
- _____ Raw data for quantitated analytes (when positively identified - including difference display, and enhanced and unenhanced spectra);
- _____ Example calculations.

NA - item not applicable to analytical procedure.



APPENDIX T

USATHAMA DATA REVIEW CHECKLIST

Lot Method Number

HOLDING TIMES YES NO N/A COMMENTS

1. Was extraction/digestion holding time met for all samples?

2. Was analysis holding time met for all extracts/digestates?

3. Were all reported dilutions performed within holding times?

PAPER TRAIL _____

4. Is chain-of-custody information present and complete?

5. Are all necessary forms present, complete, and filled out in blue or black ink?

6. Are all changes made properly, and initialed/dated?



DAILY CALIBRATIONYES NO N/ACOMMENTS

7. Was a standard curve for each analyte (as specified in the method) plus a blank analyzed with each daily lot?

8. Was a new standard curve run on the day of reanalysis of diluted extracts, and was it used for sample calculation for that date?

9. Do the calibration standards equal or bracket the concentration equivalent to the CRL and the UCR (if appropriate)?

10. Do the calibration standards equal or bracket the CRL and the highest sample or spike response in the daily lot (if appropriate)?

11. Was the standard specified in the method reanalyzed at the end of each daily lot, and at the appropriate interval within that lot and did the response meet criteria?

CONTROL SPIKES

12. Were standard matrix control spikes (spiked with the appropriate analytes and at the designated levels) and a standard matrix blank extracted/digested and analyzed on the same date as the daily lot?



YES NO N/A COMMENTS

13. If dilution and reanalysis have been performed on a different day, was at least one control spike reanalyzed with the diluted samples? Has this spike been reported with the data on the appropriate date?

14. Did control spikes pass control chart criteria? If not, has an acceptable explanation been provided, and correction taken as necessary?

SAMPLE ANALYSIS

15. Are reported sample and control spike concentrations within the certified concentration range of the method?

16. If sample concentrations above the UCR are reported, were they diluted into the certified range with the dilution factors clearly indicated?

17. Are reported detection limits the certified reporting limits?

18. Are justifications supplied for all non-use of data, analyses, etc.

19. Are all reanalyzed samples clearly marked and explanation presented?



YES NO N/A COMMENTS

20. Are all manual integration justified?

QUALITY ASSURANCE REVIEWER ONLY

21. For randomly selected data points, can the reported concentrations be back calculated using the available raw data?

REVIEWER'S SIGNATURE

CHEM: _____ DATE _____

SUPERVISOR: _____ DATE _____

QA: _____ DATE _____



APPENDIX T

USATHAMA REPORT CHECKLIST

Lot

Method Number

I have reviewed and checked the enclosed report for the following items:

Transcriptions

- ☐ 1. Soil weights and liquid volumes have been copied correctly.
- ☐ 2. All information from strip charts, chromatograms, and lab notebooks has been correctly transferred to the computer.
- ☐ 3. All information from the field chain-of-custody has been correctly copied onto the coding form.
- ☐ 4. Sample results and dilution factors derived from computer printouts or notebook calculations have been accurately copied onto the coding form.

Calculations

- ☐ 5. All calculations have been verified.
- ☐ 6. All reported values are uncorrected for moisture, dilution, or other factors.

Coding Form and QC Form

- ☐ 7. The mantissa and exponent for each sample result and dilution factor have been accurately entered onto the coding form.
- ☐ 8. The correct CRL has been used on the coding form.
- ☐ 9. The correct method ID has been noted on both the coding form and the outside of the data package.
- ☐ 10. Preparation date and analysis date on the coding form agree with those on the chain-of-custody.
- ☐ 11. The QC form indicating whether or not the QC spikes are within control has been completely and accurately completed.
- ☐ 12. Sample results are not reported below the CRL or above the highest standard.

Analyst Signature

Date

Checker Signature

Date





January 1990

USATHAMA PAM 11-41

Revision No. 0

APPENDIX U

AUDIT CHECKLIST



APPENDIX U

LABORATORY AUDIT CHECKLIST

EVALUATED LABORATORY

SUBJECT PROJECT

QC Coordinator _____

Analytical Task Manager _____

Project Manager _____

Project Officer _____

Evaluator _____

Evaluation Date _____



APPENDIX U
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?



<u>AUDIT</u> (cont)	<u>YES</u>	<u>NO</u>	<u>COMMENT</u>

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)

Instrument Maintenance?

YESNOCOMMENT

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?



<u>Data Management (cont)</u>	<u>YES</u>	<u>NO</u>	<u>COMMENT</u>
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?



January 1990

USATHAMA PAM 11-41

Revision No. 0

APPENDIX V

CALIBRATION/SURROGATE DOCUMENTATION





APPENDIX V

INSTRUCTIONS FOR CALIBRATION/SURROGATE DOCUMENTATION

FOR CALIBRATION (DAILY AND CHECK STANDARD)

1. Compound - Record the compound being monitored.
2. Check the correct box - whether daily calibration standard or check standard.
3. Method No. - Record the method number of the method being used for the designated compound.
4. Concentration - Record the target or true concentration of the standard.
5. Units - Record the units of measurements.
6. Matrix - Record the matrix of the samples being determined by the assigned method number.
7. ID - Record the identity number of the standard being monitored and the USATHAMA lot number(s) for which the calibration is applicable.
8. Date - Record the date of the measurement.
9. Low Recovery - Record the recovery of the standard if it is lower than the low specification.
10. Low Specification Value - Record the low specification value (lowest acceptable value, i.e., either the 10 percent or 25 percent or 2 S.D. criteria) for the standard in question in the box at the top of the column. Record a recovery between the low specification value and the mean in this column.
11. Mean - Record the mean recovery (labelled recovery, if applicable) in the box at the top of the column.
12. High Specification Value - Record the high specification value (highest acceptable value, i.e., either the 10 percent or 25 percent or 2 S.D. criteria) for the standard in question in the box at the top of the column. Record a recovery between the mean and the high spike in this column.
13. High Recovery - Record the recovery of the standard if it is greater than the high specification.
14. Comments - Record any comments on the measurement in this column.

Calibration data supporting multiple lots may be entered on the same form. A copy of the form shall be included in the data packages for the associated lots.



FOR SURROGATES:

1. Compound - Record the compound being monitored.
2. Check the box marked surr for surrogate.
3. Method Number - Record the method number of the method being used for the designated compound.
4. Concentration - Record the units of measurement.
5. Units - Record the units of measurement.
6. Matrix - Record the matrix of the samples being determined by the assigned method number.
7. ID - Record the individual sample numbers that the surrogate was spiked into.
8. Date - Record the date of the measurement.
9. Low Recovery - Record the recovery of the surrogate if it is lower than the low specification.
10. Low Specification - Record the low specification value (lowest acceptable value) for the surrogate in question in the box at the top of the column. Record a recovery between the low specification and the mean in this column.
11. Mean - Record the historical mean recovery of the surrogate in the box at the top of the column.
12. High Specification - Record the high specification value (highest acceptable value) for the surrogate in question in the box at the top of the column. Record a recovery between the mean and the high specification in this column.
13. High Recovery - Record the recovery of the surrogate if it is greater than the high specification.
14. Comments - Record any comments on the measurement in this column.

A separate form should be used of each surrogate in each lot. Only data from a single lot shall be included on a form. A copy of the form shall be included in the data package for that lot.



January 1990

USATHAMA PAM 11-41

Revision No. 0

APPENDIX W

FIELD SAMPLING CHECKLIST





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?



Yes ☐ No ☐ N/A ☐

6. Is there a list of accountable field documents checked out to the project coordinator? If yes, who checked them out and where is this documented?

Yes ☐ No ☐ N/A ☐

7. Is the transfer of field documents (sample tags, chain-of-custody records, logbooks, etc.) from the project coordinator to the field participants documented? If yes, where is the transfer documented?

Yes ☐ No ☐ N/A ☐

8. Have the team members received the adequate training for their position? Documented?

Yes ☐ No ☐ N/A ☐

9. Have the team members received the required number of hours of OSHA training.



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?



Yes ☐ No ☐ N/A ☐

7. Are samples collected in the types of containers specified for each type of analysis? If no, what kind of sample containers were used?

Yes ☐ No ☐ N/A ☐

8. Are samples preserved as required? If no or N/A, explain.

Yes ☐ No ☐ N/A ☐

9. Are the number, frequency, and types of samples collected as specified in the project plan or as directed by the project coordinator? If no, explain why not?

Yes ☐ No ☐ N/A ☐

10. Are samples packed for preservation when required (i.e., packed in ice, etc.)? If no or N/A, explain why.

Yes ☐ No ☐ N/A ☐

11. Is sample custody maintained at all times? How?

Yes ☐ No ☐ N/A ☐

12. Is the following information completed on each chain-of-custody record?

- Sample identification number;
- Sample collector's signature;
- Date and time of collection;
- Place and address of collection;
- Waste sample description;
- Shipper's name and address;
- Name and address of organization(s) receiving sample;



- 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, affiliation 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?



Yes ☐ No ☐ N/A ☐

17. Are glass containers with Teflon-lined screw caps used to collect the following types of samples?

- Water samples for organic analyses?
- Soil and sediment samples?
- Liquid and solid hazardous waste samples (*)?

Yes ☐ No ☐ N/A ☐

18. Are polyethylene bottles with solid polyethylene-lined caps used to collect the following types of samples?

- Water samples for metal analysis?
- Water samples for pH and fluoride analysis?
- Water samples for cyanide analysis?

Yes ☐ No ☐ N/A ☐

19. Are amber glass or aluminum foil-wrapped glass bottles used for samples suspected of being photosensitive?

* Highly alkaline wastes and wastes known to contain hydrofluoric acid should be collected in plastic containers. If it is suspected that highly alkaline materials or hydrofluoric acid is present, a small sample should be tested to determine if it reacts with the sample container.



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.



Yes ☐ No ☐ N/A ☐

2. Is a chain-of-custody record completed for all samples collected?



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 ☐

7. Were core sections which were previously etched length-wise taped with plastic caps to prevent opening during transport to the support facility?

Yes ☐ No ☐ N/A ☐

8. Were the polybutyrate line sections marked with an arrow to the top end, the boring number, and depth interval? Was a label giving the same information as well as the project name, number, the date, and the sampler's initials attached to the core in the sample handling trailer or at the site?

Yes ☐ No ☐ N/A ☐

9. Were clean polybutyrate liners placed in a clean core barrel for each additional coring increment to be drilled?

Yes ☐ No ☐ N/A ☐

10. Did the boring reach a predetermined depth or encounter the water table, whichever came first?

Yes ☐ No ☐ N/A ☐

11. For trench disposal areas was the coring performed to the maximum depth of observable contamination?

Yes ☐ No ☐ N/A ☐

12. Were all core sections transported to the support facility for logging and sample shipment preparation?



Yes ☐ No ☐ N/A ☐

13. Was the boring stake left in the ground adjacent to the borehole 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?



Yes ☐ No ☐ N/A ☐

19. Were enough augers and core barrels available so that when one set was in use a second set was being decontaminated?

Yes ☐ No ☐ N/A ☐

20. At the end of the working day did all equipment, except the drill rig, and personnel proceed to the decontamination pad where decontamination procedures were initiated?

Yes ☐ No ☐ N/A ☐

21. Were all bore cuttings drummed and stored while awaiting USATHAMA's directions for disposal?



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 ☐

7. Does information on sample tags and chain-of-custody records match?

Yes ☐ No ☐ N/A ☐

8. Does the chain-of-custody record indicate the method of sample shipment?

Yes ☐ No ☐ N/A ☐

9. Is the chain-of-custody record included with the samples in the shipping container?

Yes ☐ No ☐ N/A ☐

10. If used, do the sample traffic reports agree with the sample tags?

Yes ☐ No ☐ N/A ☐

11. If required, has a receipt for samples been provided to the facility (required by RCRA)? Describe where offer or a receipt is documented.

Yes ☐ No ☐ N/A ☐

12. If used, are blank samples identified?

Yes ☐ No ☐ N/A ☐

13. If collected, are duplicate samples identified on sample tags and chain-of-custody records?



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.)?



Yes ☐ No ☐ N/A ☐

21. If film from a self-developing camera is used, are photos matched with logbook documentation?

Yes ☐ No ☐ N/A ☐

22. Are sample tag numbers recorded? If yes, describe where they are recorded.



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?



January 1990

USATHAMA PAM 11-41

Revision No. 0

APPENDIX X
DETECTION LIMITS FOR
GC/MS
NON-CERTIFIED COMPOUNDS



Detection Limits for Non-Certified GC/MS Compounds
Volatiles

Compound	Water (ug/L)	Low Soil (ug/g)	Medium Soil (ug/g)
1. Chloromethane	10	0.01	1
2. Bromomethane	10	0.01	1
3. Vinyl Chloride	10	0.01	1
4. Chloroethane	10	0.01	1
5. Methylene Chloride	5	0.005	0.6
6. Acetone	10	0.01	1
7. Carbon Disulfide	5	0.005	0.6
8. 1,1-Dichloroethene	5	0.005	0.6
9. 1,1-Dichloroethane	5	0.005	0.6
10. 1,2-Dichloroethene (total)	5	0.005	0.6
11. Chloroform	5	0.005	0.6
12. 1,2-Dichloroethane	5	0.005	0.6
13. 2-Butanone	10	0.01	1
14. 1,1,1-Trichloroethane	5	0.005	0.6
15. Carbon Tetrachloride	5	0.005	0.6
16. Vinyl Acetate	10	0.01	1
17. Bromodichloromethane	5	0.005	0.6
18. 1,2-Dichloropropane	5	0.005	0.6
19. cis-1,3-Dichloropropene	5	0.005	0.6
20. Trichloroethene	5	0.005	0.6
21. Dibromochloromethane	5	0.005	0.6
22. 1,1,2-Trichloroethane	5	0.005	0.6
23. Benzene	5	0.005	0.6
24. trans-1,3-Dichloropropene	5	0.005	0.6
25. Bromoform	5	0.005	0.6
26. 4-Methyl-2-pentanone	10	0.01	1
27. 2-Hexanone	10	0.01	1
28. Tetrachloroethene	5	0.005	0.6
29. Toluene	5	0.005	0.6
30. 1,1,2,2-Tetrachloroethane	5	0.005	0.6
31. Chlorobenzene	5	0.005	0.6
32. Ethyl Benzene	5	0.005	0.6
33. Styrene	5	0.005	0.6
34. Xylenes (total)	5	0.005	0.6



Detection Limits for Non-Certified GC/MS Compounds
Semi-Volatiles

Compound	Water (ug/L)	Low Soil (ug/g)	Medium Soil (ug/g)
35. Phenol	10	0.3	20
36. bis(2-Chloroethyl) ether	10	0.3	20
37. 2-Chlorophenol	10	0.3	20
38. 1,3-Dichlorobenzene	10	0.3	20
39. 1,4-Dichlorobenzene	10	0.3	20
40. Benzyl Alcohol	10	0.3	20
41. 1,2-Dichlorobenzene	10	0.3	20
42. 2-Methylphenol	10	0.3	20
43. bis(2-Chloroisopropyl) ether	10	0.3	20
44. 4-Methylphenol	10	0.3	20
45. N-Nitroso-di-n- dipropylamine	10	0.3	20
46. Hexachloroethane	10	0.3	20
47. Nitrobenzene	10	0.3	20
48. Isophorone	10	0.3	20
49. 2-Nitrophenol	10	0.3	20
50. 2,4-Dimethylphenol	10	0.3	20
51. Benzoic acid	50	2	100
52. bis(2-Chloroethoxy) methane	10	0.3	20
53. 2,4-Dichlorophenol	10	0.3	20
54. 1,2,4-Trichlorobenzene	10	0.3	20
55. Naphthalene	10	0.3	20
56. 4-Chloroaniline	10	0.3	20
57. Hexachlorobutadiene	10	0.3	20
58. 4-Chloro-3-methylphenol (para-chloro-meta-cresol)	10	0.3	20
59. 2-Methylnaphthalene	10	0.3	20
60. Hexachlorocyclopentadiene	10	0.3	20
61. 2,4,6-Trichlorophenol	10	0.3	20
62. 2,4,5-Trichlorophenol	50	2	100
63. 2-Chloronaphthalene	10	0.3	20
64. 2-Nitroaniline	50	2	100
65. Dimethylphthalate	10	0.3	20
66. Acenaphthylene	10	0.3	20
67. 2,6-Dinitrotoluene	10	0.3	20
68. 3-Nitroaniline	50	2	100
69. Acenaphthene	10	0.3	20



Detection Limits for Non-Certified GC/MS Compounds
Semi-Volatiles

Compound	Water (ug/L)	Low Soil (ug/g)	Medium Soil (ug/g)
70. 2,4-Dinitrophenol	50	2	100
71. 4-Nitrophenol	50	2	100
72. Dibenzofuran	10	0.3	20
73. 2,4-Dinitrotoluene	10	0.3	20
74. Diethylphthalate	10	0.3	20
75. 4-Chlorophenyl-phenyl ether	10	0.3	20
76. Fluorene	10	0.3	20
77. 4-Nitroaniline	50	2	100
78. 4,6-Dinitro-2-methylphenol	50	2	100
79. N-nitrosodiphenylamine	10	0.3	20
80. 4-Bromophenyl-phenylether	10	0.3	20
81. Hexachlorobenzene	10	0.3	20
82. Pentachlorophenol	50	2	100
83. Phenanthrene	10	0.3	20
84. Anthracene	10	0.3	20
85. Di-n-butylphthalate	10	0.3	20
86. Fluoranthene	10	0.3	20
87. Pyrene	10	0.3	20
88. Butylbenzylphthalate	10	0.3	20
89. 3,3'-Dichlorobenzidine	20	0.7	40
90. Benzo(a)anthracene	10	0.3	20
91. Chrysene	10	0.3	20
92. bis(2-Ethylhexyl)phthalate	10	0.3	20
93. Di-n-octylphthalate	10	0.3	20
94. Benzo(b)fluoranthene	10	0.3	20
95. Benzo(k)fluoranthene	10	0.3	20
96. Benzo(a)pyrene	10	0.3	20
97. Indeno(1,2,3-cd)pyrene	10	0.3	20
98. Dibenz(a,h)anthracene	10	0.3	20
99. Benzo(g,h,i)perylene	10	0.3	20



Detection Limits for Non-Certified GC/MS Compounds
Pesticides/PCBs

Compound	Water (ug/L)	Low Soil (ug/g)	Medium Soil (ug/g)
100. alpha-BHC	3	0.5	6
101. beta-BHC	3	0.5	6
102. delta-BHC	3	0.5	6
103. gamma-BHC (Lindane)	3	0.5	6
104. Heptachlor	3	0.5	6
105. Aldrin	3	0.5	6
106. Heptachlor epoxide	3	0.5	6
107. Endosulfan I	3	0.5	6
108. Dieldrin	6	1.0	10
109. 4,4'-DDE	6	1.0	10
110. Endrin	6	1.0	10
111. Endosulfan II	6	1.0	10
112. 4,4'-DDD	6	1.0	10
113. Endosulfan sulfate	6	1.0	10
114. 4,4'-DDT	6	1.0	10
115. Methoxychlor	30	5	60
116. Endrin ketone	6	1.0	10
117. alpha-Chlordane	30	5	60
118. gamma-Chlordane	30	5	60
119. Toxaphene	60	10	100
120. PCB-1016	30	5	60
121. PCB-1221	30	5	60
122. PCB-1232	30	5	60
123. PCB-1242	30	5	60
124. PCB-1248	30	5	60
125. PCB-1254	60	10	100
126. PCB-1260	60	10	100





APPENDIX Y
REJECTION OF OUTLIERS
FROM
CERTIFICATION DATA





APPENDIX Y

REJECTION OF OUTLIERS FROM CERTIFICATION DATA

Since one widely divergent datum can invalidate an entire certification data set, all such results should be plotted and inspected for visual evidence of outliers (extreme values). For Class 1 and 1B certification with a minimum of four replicate responses at each concentration Dixon's Outlier Test with $\alpha = 0.05$ (Appendix K) should be applied directly to a suspect value. Rejection requires exceeding the critical value of r at the 95 percent confidence level (Table K-1). No more than one datum can be rejected at a given concentration and no more than two values total should be rejected from a set. If two rejected values originated on the same day, a repeat of that day's certification should be performed.

For Class 1A certification, no more than one outlier can be rejected from a set. To produce an adequate number of values to apply Dixon's Test, at least two sets of duplicates should be normalized by conversion to percentage recovery (the pair with a suspect value plus a nearest neighbor pair). When the suspect pair has neighbors on each side, all six values should be converted to percentage recovery prior to application of Dixon's Test.

When an outlier has been replaced, LOF and ZI tests require adjustment of the degrees of freedom to compensate for the loss, since any replacement value would be calculated and, therefore, does not contribute to the associated degrees of freedom.

With small data sets such as are available from most certifications, it will be necessary to replace a rejected datum with a most probable value. This can be done from the following relationship:

$$\text{dummy value} = \text{row mean} + \text{column mean} - \text{grand mean}$$

<u>Target Value</u>	<u>Found Value 1</u>	<u>Found Value 2</u>
0.5 x	A	E
2 x	B	F
10 x	C	G
50 x	D	H

Calculated outlier by Dixon's Test at $\alpha = 0.05$



The replacement value for C is calculated according to the following:

Replacement value (X) =

$$\frac{X + G}{2} + \frac{A + B + X + D}{4} - \frac{A + B + X + D + E + F + G + H}{8}$$

Row Mean Column Mean Grand Mean

Multiplying through by 8 and rearranging results in

$$X(8 - 4 - 2 + 1) = (G)(4) + (A + B + D)(2) - (A + B + D + E + F + G + H)$$

or

$$X = \frac{(G)(4) + (A + B + D)(2) - (A + B + D + E + F + G + H)}{3}$$

The value of X can then be used to replace C in the example data set.



INDEX

Absolute Calibration	13.4
Accuracy	5.7 14.2.3
Acidity	5.2.2
Alkalinity	5.2.2
Analytical Reference Materials	3.3
Analytical Methods	5.2 Appendix A
Asbestos	5.2.2
Audit Checklist	12.1 Appendix U
Audits, External	12.1
Audits, Internal	12.2
Audits, Performance	12.0
Audits, System	12.0
Biochemical Oxygen Demand(BOD)	5.2.2
Calibration Check Standards	8.2.1 8.2.2 8.2.3
Calibration Curves	8.1
Calibration Documentation	Appendix V
Calibration Frequency Schedule	13.3
Calibration Identification	13.1
Calibration Standards	13.2
Case File	10.5
Central Line	11.4.1 11.4.2



Certification	5.1 5.4
Certification Data Packages	5.1 14.3
Certification Data Packages	
Checklist	Appendix P
Certification Method Format	Appendix A
Certification Program Output	Appendix C
Certification Samples	5.6
Certified Check Standards	5.3
	8.2
Certified Range	5.7.1
Certified Reporting Limit (CRL)	5.7.2 8.1.3 8.1.4 11.3.1 14.2.2
Chain-of-Custody (COC)	4.1 4.2.1 6.11.1 7.0 7.4 7.5 7.6 10.0 10.5.1.2
Chemical Oxygen Demand (COD)	5.2.2
Chemistry Branch	4.1 5.2.1 5.2.3 5.3 5.4 5.6.2 10.6 14.2.1



Class 1 Certification	5.3 5.7 5.7.2 10.4.1 11.2.3 11.3.1
Class 1A Certification	5.3 5.7 5.7.2 10.4.1 11.2.3 11.3.1 11.4
Class 1B Certification	5.3 5.7 5.7.2 10.4.1 11.2.3 11.3.1 11.4
Class 2 Certification	5.2 5.3 5.7 5.7.3 10.4.2 11.2.3 11.3.2 11.4
Cleaning Procedures (Sample bottles)	6.3 Appendix F
Concentration Range	5.7.1
Conductivity	5.2.2
Containers	6.3 Appendix H
Contract Laboratory Program (CLP)	5.2.2
Contracting Officer's Representative	4.5.1
Contractor Analytical Task Manager	4.1 4.3 4.4



Contractor Quality Assurance Coordinator (QAC)	4.1 4.3 4.4
Contractor QAC Checklist	4.4 Appendix R
Contractor Project Manager	4.1 4.3 5.3
Control Analytes	11.1 11.2.3
Control Charts	4.4 11.2.3 11.3.1 11.4
Control Chart Checklist	Appendix Q
Control Samples	11.2
Control Samples, Concentration	11.2.3
Control Samples, Frequency	11.2.3
Control Samples, Preparation of	11.2.2
Corrective Actions	10.5.1.2 10.5.1.3 11.5 11.5.2 15.0
Criterion of Detection (COD)	14.2.2
Daily Calibration	5.7.2 8.1.2
Data Deliverables	10.5
Data Management System	10.6
Data Order Package	10.5
Data Package	10.5 10.5.1.2



Data Package Checklist	4.4 Appendix T
Data Package Review	10.5.1.3
Data Quality	4.5.3
Data Reduction	10.0
Data Reporting	10.0 10.4 10.7
Data Reporting, QC	11.3
Data Review	10.8
Data Validation	10.0 10.8
Decertification	5.5
Detection Limits for GC/MS Non-certified Compounds	Appendix X
Dilutions	11.3.1
Dissolved Organic Carbon (DOC)	5.2.2
Dixon's Outlier Test	11.4.1 11.4.2 Appendix K
Document Control Procedures	10.5.1
Documentation	14.3
Extended Range Certifications	11.2.3
Evidentiary Considerations	7.7
Field Detection Methods	5.2.1
Field Equipment	6.5
Field Operations Standing Operating Procedures	Appendix G
Field Sampling Checklist	Appendix W



Flagging Codes	10.5.1.2 10.7 11.2.3 14.2.2
Forms	10.5.1.5
Gas Chromatography/Mass Spectrometry (GC/MS)	5.7
Group Check	10.6
Hardness	5.2.2
Holding Times	11.5.1
Initial Calibration	5.7.2 8.1.1 8.1.3
Instrument Calibration	5.7.2 5.7.3 8.1
Instrument Logs	4.4
Installation Restoration Data Management System (IRDMS)	4.4 10.6
Instrument Maintenance	13.0
Instrumental Detection Limit	14.2.2
Interim Reference Material (IRMs)	8.3.2
Internal Quality Control Checks	11.0
Laboratory's Internal Number System	6.12
Laboratory Operations (SOP)	Appendix J
Lack-of-Fit (LOF)	5.3 14.2.1 Appendix B
Logbooks	10.1 10.3 10.5.1.4



Lot	4.4 6.12
Low Throughput Methods	5.7
Lower Control Limits	11.2.3 11.4.1 11.4.2
Lower Warning Limits	11.4.1 11.4.2
Maintenance Control Charts	4.4
Master Stock Solutions	5.6.2 5.7.2
Matrix Spike	11.2.3
Matrix Spike Duplicates	11.2.3
Method Blank Corrections	11.3.1
Method Development	5.2.3
Method Development Documentation	Appendix D
Method Number	5.2.3
Modified Control Limits	11.4.1 11.5 11.5.2 Appendix O
Monitor Wells	6.5.1
Multi-Analyte Methods	8.2.3 11.0 11.2.3
Natural Matrix Spikes	11.2.3
Natural Matrix Surrogate Spikes	11.2.3
Non-Detect (ND)	10.7
Notebooks	10.5.1.4
Off-the-Shelf Materials	8.3.3



Oil and Grease	5.2.2
Out-of-Control Situations	11.5 11.5.1
Outlier Test	Appendix K
Outliers-Certification	Appendix Y
Percent Imprecision	14.2.6
Percent Inaccuracy	14.2.5
Percent Moisture	9.3.2
Personnel Qualifications	5.4,6.2
pH	5.2.2
Precertification Calibration	5.3
Precertification Data Packages	5.1 5.3
Precertification Data Package Checklist	Appendix P
Precertification Method Format	Appendix A
Precertification Program Output	Appendix C
Project Officer	4.4 5.3
Project QC Plan	4.5
Quality Assurance Reports	16.0
Quantitation Limit	10.7
R Control Charts	11.5.3
Range Extensions	5.7.1
Rank Sum Test	5.7.3 Appendix E
Reanalysis	4.5.3
Record Check	10.6



Reference Material	8.3 10.3
Resampling	4.5.3
Rounding	10.4
Salinity	5.2.2
Sample Analysis	9.4
Sample Collection	7.3
Sample Containers Cleaning Procedure	Appendix F
Sample Dilution	5.7.1 9.4 11.3.1
Sample Filtration	6.6 9.3 9.3.1
Sample Handling	6.11.2 7.3 10.3
Sample Holding	9.2 Appendix H
Sample Identification	6.12 7.3 10.2.1
Sample Logging	10.2.1
Sample Preparation	9.3
Sample Preservation	6.9 Appendix H
Sample Receipt Checklist	Appendix S
Sample Shipment	7.4
Sampling Logs	4.4



Sampling Instructions	4.5.3 6.4.1 6.4.2 6.4.3 6.5 6.5.1 6.5.2
Second Column Confirmation	5.2 9.4
Sediments	6.8 9.3.2
Significant Figures	5.7.2 10.4 14.2
Single Day X-R Control Charts	11.4.1
Soil	6.7 9.3.2
Spiking Solution Control	Appendix N
Standard Analytical Methods	5.2
Standard Analytical Reference Material (SARMs)	8.3.1 Appendix I
Standard Deviation	14.2.4
Standard Matrix Spikes	5.4 11.2 11.2.3
Standard Soil Samples	5.6.2
Standard Water Samples	5.6.1
Standing Operating Procedure (SOP)	6.10 9.1
Statistical Analysis of Certification Data	14.1
Statistical Analysis of Precertification Data	14.2
Subcontractor Laboratory	4.5



Surface Water	6.6 9.3.1
Surrogates	11.2.3
Surrogate Documentation	Appendix V
Survey Planning and Preparation	7.2
Tap Water Samples	6.4.2 9.3.1
Target Reporting Limits (TRL)	4.2.1 5.3 5.7.1 5.7.3
Temperature	5.2.2
Three Point Moving Average Control Chart	11.4.2
Total Dissolved Solids (TDS)	5.2.2
Total Organic Carbon (TOC)	5.2.2
Total Organic Halogen (TOX)	5.2.2
Total Petroleum Hydrocarbons (TPH)	5.2.2
Total Solids (TS)	5.2.2
Total Suspended Solids (TSS)	5.2.2
Training	4.5.3 6.2 6.7 6.8
Transfer-of-Custody	7.4
Truncation	14.2.2
Upper Control Limits	11.2.3
Upper Warning Limits	11.4.1
User's Guide	10.6
Volatiles	6.4



Water Supply Wells	6.5.2
Working Standards	10.3
X Control Charts	11.5.2
X-R Control Charts for Duplicate Spike Recovery	Appendix L
X-R Control Chart for 3-Point Moving Average Spike Recovery	Appendix M
Zero Intercept (ZI)	5.3 14.2.1 Appendix B



USER EVALUATION SHEET/CHANGE OF ADDRESS

USATHAMA undertakes a continuing effort to improve the quality of its Quality Assurance Program. Your comments will aid us in achieving our goals. (Additional sheets may be attached.)

1. Organization (The following comments are provided concerning the organization of the Program).

2. Useability (The following comments are provided as to the ability to find items in the Program).

3. Concepts (The following comments are provided as to the existing concepts of the Program or to recommend new or innovative concepts).

4. General (The following specific comments are offered for consideration in updates to the Program).

5. _____
Name

Organization

Current Address _____
Address

City, State, Zip

Telephone



6. If indicating a change of address or address correction, please provide the new or correct address in block 5 above and the old or incorrect address below.

Name

Organization

Old

Address _____
Address

City, State, Zip

Telephone

Mail completed form to:

Commander
U.S. Army Toxic and Hazardous Materials Agency
ATTN: CETHA-TS-C
Aberdeen Proving Ground, MD 21010-5401

