Round-Robin Study of Methods for Trace Metal Analysis

Graphite Furnace Atomic Absorption Spectroscopy-Cadmium, Arsenic, and Chromium

TR-108989

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REPORT SUMMARY

Eighteen utility laboratories evaluated graphite furnace atomic absorption spectroscopy (GFAAS) methods for measuring cadmium, arsenic, and chromium in a variety of utility aqueous streams. This EPRI Tailored Collaboration Project, part of the ongoing Analytical Methods Qualification (AMQ) program, will help utilities define reasonable pollutant discharge limits and effluent monitoring requirements.

BACKGROUND

Federal and state permits are requiring electric utilities to monitor power plant effluents for increasingly low concentrations of trace metals, in some cases at levels that preclude reliable measurement. A central source of verified data on the standard deviation, recovery, and quantification levels for various methods would help utilities define reasonable effluent guidelines and monitoring requirements. It would also aid in the selection of appropriate analytical methods. EPRI sponsored this work to evaluate EPA GFAAS methods 213.2 (cadmium), 206.2 (arsenic), and 218.2 (chromium).

OBJECTIVE

To verify the standard deviation, recovery, and Alternative Minimum Level (AML) for measurement of specific trace metals in typical utility aqueous samples.

APPROACH

Investigators developed a test program based on ASTM D2777-96 protocols. At utility test sites, they collected several types of water samples (Midwest groundwater, acid mine drainage, and estuarine), they then injected cadmium, arsenic, and chromium into them. Eighteen utility laboratories conducted round-robin tests on these samples using EPA analytical methods. Based on the test results, the investigators developed single-operator (one laboratory) and multiple-operator (overall) standard deviation data for each element and sample matrix combination. They derived estimates of the Interlaboratory Critical Level (L_{CI}), Interlaboratory Detection Level (L_{DI}) and AML for each element in each matrix. They compared these values with concentrations specified by EPA and with federal Water Quality Criteria (WQC).

RESULTS

The L_{CI}, L_{DI} and AML were calculated for each trace element in each water type. Only three of the 12 element/matrix combinations had AMLs lower than the lowest freshwater EPA WQC: arsenic in reagent grade water, groundwater, and estuarine. No cases were found in which the Interlaboratory Detection Level (L_{DI}) or the AML was lower than the EPA Detection Limit (DL) quoted in the analytical method.

EPRI PERSPECTIVE

This report is the fifth (AMQ-IV, Round 2) in a series of comprehensive, round-robin evaluations to verify methods for chemical analysis. EPRI report CS-5910, Volumes 1- 3, and TR-105910 contain details of four similar round-robin studies of atomic absorption methods for 18 elements. EPRI report TR-106220 discussed in detail the development of the Alternative Minimum Level, presented AML values calculated from the data collected in all of the previous AMQ round-robin studies, and included a program on diskette to calculate AMLs. EPRI, in conjunction with the Utility Water Act Group, continues to work with the Inter-Industry Analytical Group (IIAG), a broad coalition of industry groups, ASTM, and EPA to achieve consensus on detection and quantification limits appropriate for NPDES permit compliance monitoring.

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ABSTRACT

The objective of the Analytical Methods Qualification (AMQ) phase of the RP1851 project is to develop validated standard deviation and bias statements of analytical methods for selected elements in utility matrices. During AMQ-IV, Round 2, three elements (cadmium, arsenic and chromium) were validated in four matrices (reagent grade water, midwest groundwater, acid mine drainage, and estuarine water). The graphite furnace methods validated were Method 213.2 (cadmium), Method 206.2 (arsenic) and Method 218.2 (chromium) from the Metals - Atomic Absorption Methods in EPA 600/4-79-020 Methods for Chemical Analysis of Water and Wastes (March 1983 Revision). Eighteen laboratories completed the study.

Statements of standard deviation and bias for each element and matrix were produced using STATCALC, a statistical analysis program developed by EPRI based on ASTM D2777. The standard deviation data were used to calculate the Interlaboratory Critical Level (L_{CI}), Interlaboratory Detection Level (L_{DI}) and Alternative Minimum Level (AML) for each element by matrix. The Interlaboratory Critical Level is the lowest concentration that is distinct from zero to a specific level of confidence. The Interlaboratory Detection Level is the concentration at which a given analytical procedure may be relied upon to lead to detection. The Alternative Minimum Level, which is an estimate of quantification, is a factor of 10 times the interlaboratory standard deviation at the L_{CI} corrected to true concentration units with the appropriate prediction interval. In comparing the AMLs calculated from this study with the lowest EPA water quality criteria (WQC) listed for freshwater, the AMLs were higher in 9 of the 12 cases.

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CONTENTS

---

1 INTRODUCTION 1-1
1.1 Background And Objectives Of The Analytical Methods Qualification Project....1-1
1.1.1 *Regulatory Environment*...*1-1*
1.1.2 *AMQ Design and Objectives* *1-1*
1.1.3 *Use of Validation Data*..*1-2*
1.2 Overview of AMQ-IV Round 2...1-5
1.3 Objectives Of This Report...1-5
1.4 Use Of This Report 1-5
1.5 Organization of this Report 1-5
1.6 References 1-6

2 SELECTION OF PARAMETERS FOR VALIDATION TESTING 2-1
2.1 Selection of Elements 2-1
2.2 Selection of Test Methods and Procedures 2-2
2.3 Selection of Test Matrices..2-4
2.4 Selection of Test Concentrations..2-5
2.5 References 2-9

3 LABORATORY SELECTION FOR AMQ-IV ROUND 2 3-1
3.1 Solicitation Process..3-1
3.2 Laboratory Selection Process 3-1

4 AMQ-IV ROUND 2 SAMPLE PREPARATION AND DISBURSEMENT 4-1
4.1 Spiking Hardware Checkout and Equipment Calibration 4-1
4.2 Sample Collection/Stabilization...4-3
4.2.1 *Groundwater Sample Collection*...*4-3*
4.2.2 Estuarine Sample Collection *4-3*
4.3 Test Matrix Characterization 4-5
4.4 Procedures For Sample Processing 4-7

4.4.1 *Sample Tracking System*........4-8
4.4.2 *Sample Filling Procedure*........4-10
4.4.3 *Packaging Samples for Disbursement to Participating Laboratories*........4-15
4.4.4 *Shipping of Samples to the Participating Laboratories*........4-18
4.5 Instructions To Participating Laboratories........4-18

5 QUALITY ASSURANCE/QUALITY CONTROL........5-1
5.1 Analyses to Verify AMQ-IV Round 2 Sample Concentrations........5-1
5.2 Analyses to Confirm Stability in AMQ-IV Round 2........5-2

6 AMQ STATISTICAL ANALYSIS PROGRAM........6-1
6.1 STATCALC Collaborative Statistical Analysis Program........6-1
6.1.1 *Notation for STATCALC*........6-4
6.1.2 *Data Notation*........6-5
6.2 Data Validation........6-7
6.2.1 *"Zero" Data*........6-7
6.2.2 *Censored or "Less Than" Data*........6-7
6.2.3 *"Negative" Data*........6-8
6.3 “Factor of 5” Data Screening........6-8
6.3.1 *The Screening Procedure*........6-8
6.4 Lab Ranking........6-9
6.4.1 *Rationale for the Test*........6-9
6.4.2 *Discussion of the Test*........6-9
6.4.3 *Justification for Use of the Test*........6-11
6.5 Testing for Outliers........6-11
6.5.1 *Rationale for the Test*........6-11
6.5.2 *Discussion of the Test*........6-12
6.5.3 *Justification for the Procedure*........6-13
6.6 Testing for Normality........6-13
6.6.1 *The Shapiro-Wilk (W) Test (Sample Size <= 50)*........6-14
6.6.2 *D'Agostino's (D) Test (Sample Size > 50)*........6-15
6.7 Calculation of Analytical Method Performance Statistics........6-17
6.7.1 *Calculation of Method Mean Recovery and Bias*........6-18
6.7.2 *Calculation of Method Precision Statistics (Standard Deviations)*........6-19
6.8 Testing for Significant Bias........6-29
6.8.1 *General*........6-29

6.8.2 *Rationale for the Procedure* *6-29*
6.8.3 *Outline of the Calculations* *6-29*
6.9 Use of STATCALC Output 6-30
6.10 References 6-31

7 DATA EVALUATION 7-1
7.1 Operating Data 7-1
7.1.1 *Personnel Experience Levels* *7-1*
7.1.2 *Analytical Instrumentation* *7-3*
7.1.3 *Laboratory Standards and Sample Handling* *7-4*
7.1.4 *Sample Preparation and Analysis* *7-4*
7.2 Raw Data Analysis 7-4
7.2.1 *Raw Data* *7-4*
7.2.2 *Outlier Removal Results* *7-4*
7.2.3 *Normality Testing* *7-6*
7.3 Reduced AMQ-IV Round 2 Data 7-7
7.3.1 *Arsenic* *7-7*
7.3.2 *Cadmium* *7-9*
7.3.3 *Chromium* *7-16*
7.4 References 7-24

8 ALTERNATIVE MINIMUM LEVEL 8-1
8.1 Technical Approaches to Detection and Quantification Levels for Demonstrating Regulatory Compliance 8-2
8.1.1 *The Detection Problem* *8-2*
8.1.2 *The Quantification Problem* *8-4*
8.1.3 *Calibration Curve Methods for Computing Detection and Quantification Levels* *8-6*
8.2 EPA Definitions of Detection and Quantification and Their Problems 8-6
8.3 Modeling Standard Deviation Data 8-10
8.4 Alternative Minimum Level 8-12
8.4.1 *Background and Overview* *8-12*
8.4.2 *Computation of the AML from Interlaboratory Data* *8-14*
8.5 Determining Regulatory Compliance 8-20
8.5.1 *Regulatory Compliance Limit Greater Than or Equal to the Quantification Level* *8-20*
8.5.2 *Regulatory Compliance Limit Below the Quantification Level* *8-20*

8.6 ASTM Interlaboratory Detection Estimate (IDE) 8-21
8.7 Acknowledgments..8-22
8.8 References 8-22

9 SUMMARY OF AMLS COMPUTED FROM THE TEST DATA 9-1
9.1 Arsenic...9-2
9.2 Cadmium..9-3
9.3 Chromium 9-4
9.4 References 9-5

10 CONCLUSIONS 10-1

***A* NOMENCLATURE...A-1**

***B* LABORATORY CONTACT WORKSHEET B-1**

***C* INSTRUCTIONS TO PARTICIPANTS..C-1**

***D* METHOD PARAMETERS REPORTING FORM...D-1**

***E* HIGHLIGHTS OF LAB OPERATING DATA SURVEY E-1**

***F* LABORATORY DATA REPORTING FORM F-1**

***G* RAW DATA G-1**

***H* STATCALC INPUT/OUTPUT H-1**

1

INTRODUCTION

1.1 Background And Objectives Of The Analytical Methods Qualification Project

1.1.1 *Regulatory Environment*

The utility industry is required under the Clean Water Act (Federal Water Pollution Control Act) as amended to monitor their discharges for numerous chemical substances. The discharge limits vary with each pollutant. Where limits are set below levels at which quantification is possible, compliance in many states is gauged exclusively on the basis of monitoring results at or above the quantification level. An exception applies to limits expressed in terms of "no detectable discharge," where the detection limit often is used to gauge compliance. Concerns have arisen within the industry because the detection limits published in the USEPA MCAW (Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Revised March 1983) are based on signal-to-noise ratios rather than detection limits that take into account all sources of interferences that are present when the test method is used in practice. If compliance standards, such as NPDES permit limitations, are set at levels at which it is not possible to make reliable measurements, permittees may be subjected to harsh civil and criminal enforcement consequences entirely as a result of analytical variability, as opposed to an unacceptable concentration of pollutants in their effluents. That is because compliance is gauged solely on the basis of the analytical results of a permittee's effluent, not on the pollution control measures employed. Unless appropriate detection and quantification levels are developed and applied, permittees may experience compliance problems, notwithstanding their best efforts to select and apply effective pollution control measures.

1.1.2 *AMQ Design and Objectives*

EPRI Project RP1851, "Utility Aqueous Discharge Monitoring - Analytical Methods Qualification," (AMQ) was initiated in 1981 to improve the industry's ability to monitor plant wastewater streams. The project was divided into two phases - a literature review and a series of field studies. The goal of the first phase was to identify pollutants of concern to the electric utility industry and to document state-of-the-art analytical methods used to monitor the pollutants. Of special interest were regulated pollutants for which little analytical data had been collected. The literature study revealed that the EPA analytical method validation data were often obtained for matrices and concentrations not representative of the steam electric industry. These findings prompted a field study program to validate the analytical methods used for discharge monitoring.

The primary objective of the AMQ project is to collect precision (standard deviation) and bias (observed value minus true value) data for methods used to determine selected parameters and elements in utility discharge streams. The field study was comprised of round-robin collaborative testing using representative utility laboratories and actual utility discharge streams. A round-robin study consists of distributing identical whole volume samples to individual laboratories for analysis according to a specified method. The analytical methods validated were from the USEPA MCAW (Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, Revised March 1983), which are approved by EPA for compliance testing under 40 CFR Part 136. The studies followed the experimental design recommended by the American Society for Testing and Materials' "Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water," D2777, for interlaboratory round-robin studies.

Table 1-1 provides an overview of the entire AMQ project, which was divided into four parts in order to facilitate participation by industry laboratories and to permit modification of the test design to reflect changing environmental issues or regulatory requirements. The elements and parameters in each part were selected on the basis of their importance to the utility industry and regulatory interest. All work up through AMQ-IV Round 1 was funded under Research Project RP1851. The current project, a Tailored Collaboration effort, was funded under Work Order WO3569-01.

1.1.3 *Use of Validation Data*

One of the primary objectives of the AMQ project is to establish estimates of detection and quantification for use in compliance monitoring. A number of definitions of detection and quantification limits/levels have been published over the years, and the definitions have continued to evolve. The pioneering work of Currie (1) forms the basis of most, if not all, of the various approaches. For the reports published for AMQ-I, -II, -III and -IV, AMQ researchers evaluated the various definitions available and selected ones that had a strong technical justification and that incorporated the use of interlaboratory data. A discussion of the various definitions examined, the rationale for selection of the ones used and the values calculated using the definitions can be found in the EPRI reports cited in Table 1-1.

During the summer of 1995, EPRI along with the Inter-Industry Analytical Group (IIAG), an industry coalition, conducted an extensive review of available detection and quantification level definitions (2). This evaluation produced two major outputs:

- A list of properties and performance standards to evaluate detection and quantification level definitions, and

- A consensus agreement on an Alternative Minimum Level (AML) to estimate a method's quantification level.

EPRI worked within the industry coalition to develop a definition called the Alternative Minimum Level (AML). The AML, which is an estimate of the quantification level, is defined as 10 times the interlaboratory standard deviation at the lowest concentration that is differentiable from zero, the Interlaboratory Critical Level (L_{CI}). The Interlaboratory Detection Level (L_{DI}) is defined as the point at which a given analytical procedure may be relied upon to lead to a detection. The development of these definitions, and the computational approach for the L_{CI}, L_{DI} and the AML are discussed in Section 8. The standard deviation data obtained by this study were used to calculate for each element by matrix the values for L_{CI}, L_{DI} and AML that are found in Section 9. These values provide a realistic estimate of the capabilities of EPA-approved analytical methods in the compliance monitoring situation in utility aqueous matrices tested.

Table 1-1
Utility Aqueous Discharge Monitoring - Analytical Methods Qualification (AMQ) Program Overview

Project Title	Part	Round	Parameters	Method	EPRI Report
Sampling and Analysis of Utility Pollutants	*		---	---	CS-3741
Analytical Methods Qualification	I	1	As, Se	GFAAS**	CS-5910
		2	Cr, Cu, Ni, Pb	GFAAS	Vol. 1
Analytical Methods Qualification	II		Hg	CVAAS	CS-5910
			Fe, Zn	Flame AAS	Vol. 2
			Cd	GFAAS	
Analytical Methods Qualification	III		Al, Ba, Be, B, Cd, Cr, Cu, Fe, Pb, Mn, Mo, Ni, V, Zn	ICP-AES	CS-5910 Vol. 3
Analytical Methods Qualification	IV	1	Al, Be, Tl	GFAAS	TR-105910
		2***	Cd, As, Cr	GFAAS	**This Report**

* Initial effort under EPRI Project RP1851 which involved collection and analysis of data on discharge rates and data on the analytical precision and bias for utility discharge species.

** Several seawater laboratories determined As and Se by GHAAS.

*** Tailored Collaboration effort funded under WO3569-01.

GFAAS = Graphite Furnace Atomic Absorption Spectroscopy

GHAAS = Gaseous Hydride AAS

CVAAS = Cold Vapor AAS

ICP-AES = Inductively Coupled Plasma - Atomic Emission Spectroscopy

1.2 Overview of AMQ-IV Round 2

The AMQ project is based on the premise that a method qualification project should use matrices representative of those encountered by the analyst in routine work. Furthermore, since the shipment and storage of samples is part of the normal analysis procedure at most laboratories and comparison of the results from different laboratories on split samples is often encountered in compliance monitoring, the test program should include spiking the matrices and sending aliquots to each participant.

The AMQ test matrices were selected to be of interest to the utility industry. Descriptions of the matrices selected and the reasons for selecting those matrices are found in Section 2. The elements selected for validation in AMQ-IV Round 2 were cadmium, arsenic and chromium. The EPA Graphite Furnace Atomic Absorption Spectroscopy methods for each element were selected for validation.

1.3 Objectives Of This Report

The objective of this report is to provide the utility personnel with validated standard deviation and bias data for cadmium, arsenic and chromium by the EPA-approved GFAAS methods for cadmium (213.2), arsenic (206.2) and chromium (218.2) contained in the USEPA MCAW. In addition, we have provided estimates of the method's Interlaboratory Critical Level (L_{CI}) and Alternative Minimum Level (AML) for each element in each matrix based on the data collected.

1.4 Use Of This Report

When an analyst produces a result that falls below the Alternative Minimum Level (AML), the EPRI quantification level definition, the result needs to be evaluated carefully in terms of its use. It is important that the use of such data in a regulatory setting be coupled with a thorough understanding of the analytical variability associated with the data. The intent of this report is to provide utilities with detection and quantification levels based on measurements made in qualified laboratories using utility matrices. The L_{CI}s, L_{DI}s and AMLs derived from this interlaboratory data provide a framework for evaluating data to be used in permit negotiation and compliance monitoring situations.

1.5 Organization of this Report

The methodology used in selecting parameters for testing is discussed in Section 2. Section 3 describes the solicitation process used to enlist the volunteer laboratories. Also included in this section is a list of the participants. The sample collection, spiking, and disbursement procedures are described in Section 4, along with the laboratory reporting requirements. Section 5 summarizes the quality assurance approach and the results of analyses performed to verify sample integrity. In Section 6, a discussion of the statistical methods applied to the data is presented. The complete data evaluation process is described in Section 7, and in Section 8 the development of detection and quantification definitions for compliance monitoring are discussed. Section 9 contains the Alternative Minimum Levels calculated from the AMQ-IV Round 2 data. The report's conclusions are given in Section 10. The appendices contain the instructions given to the laboratories, operating data reported by the laboratories and the analytical results summarized by element in tabular form.

1.6 References

1. Currie, L.A (1968). Limits for Qualitative Detection and Quantitative Determination: Application to Radiochemistry. Analytical Chemistry, 40, 586-593.

2. Koorse, S. J., "Industry Presentation for EPA's Meeting on the Draft 'National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-based Effluent Limitations Set Below Analytical Detection/Quantitation Levels'", submitted to the EPA on June 21, 1995 on behalf of a coalition of American Industries by law firm of Hunton & Williams.

2

SELECTION OF PARAMETERS FOR VALIDATION TESTING

The methodology used in selecting elements, methods, test concentrations and matrices is discussed in the following sections.

2.1 Selection of Elements

For the AMQ project, only metals were considered since data gathered for the Sampling and Analysis of Utility Pollutants (EPRI Report CS-3741) project showed that organics are rarely found in steam electric power plant discharges. As indicated in Table 1-1, a number of metals were investigated in earlier AMQ studies. For the most part, the elements selected were included for regulatory interest, direct importance as a discharged pollutant, potential importance in the groundwater monitoring programs and lack of previous AMQ validation.

A survey was conducted among members of the RP1851 Project Advisory Committee to solicit information on the elements and matrices of interest to electric utilities. Table 2-1 summarizes the level of interest of various metals, listed in order from highest interest to lowest. Based on discussion with the Project Advisory Committee, cadmium, arsenic and chromium were selected for validation by GFAAS in this round.

Table 2-1
Survey Results -Level of Interest in Elements

Element	Level of Interest
Hg	High
Cd	High
As	High
Se	High
Pb	High

Table 2-1
Survey Results -Level of Interest in Elements

Element	Level of Interest
Ag	Medium
Ni	Medium
Mn	Medium
Cr^{+3}	Medium
Ba	Medium
Sb	Medium
Cr^{+6}	Medium
Mg	Medium
B	Low
V	Low
Cu	Low

2.2 Selection of Test Methods and Procedures

The GFAAS methods selected for validation in AMQ-IV Round 2 were Method 213.2 (cadmium), Method 206.2 (arsenic) and Method 218.2 (chromium) for "Atomic Absorption, Furnace Technique" from the Metals - Atomic Absorption Methods in EPA 600/4-79-020 Methods for Chemical Analysis of Water and Wastes (March 1983 revision). The digestion procedure listed in Method 206.2 specifies that hydrogen peroxide and nitric acid be used in the digestion of samples for arsenic analysis. The cadmium and chromium methods require only nitric acid. Using two different digestion procedures would significantly increase the participants' workload and the volume of sample that each laboratory would require. TRW conducted a digestion comparison to determine the necessity of digesting the samples with hydrogen peroxide for arsenic analysis. An aliquot of river water from a previous AMQ study was spiked with arsenic, cadmium and chromium and split. Duplicate samples were digested using only nitric acid and both nitric acid and hydrogen peroxide. Unspiked duplicate blanks were digested in the same manner. The digested samples were split and analyzed by Inductively Coupled Plasma - Mass Spectrometry. As Table 2-2 shows, no differences in recoveries were noted.

Table 2-2
Comparison of Recoveries for Nitric Acid Digestion and Hydrogen Peroxide Digestion for Arsenic, Cadmium and Chromium in Spiked River Water

Sample	Measured, Blank µg/L	Measured, Spiked µg/L	Added Spike, µg/L	Recovery
As, HNO_3 Digestion	1.0	89.2	82.2	107%
As, H_2O_2/HNO_3 Digestion	1.1	88.9	82.2	107%
Cd, HNO_3 Digestion	0.1	7.4	6.8	107%
Cd, H_2O_2/HNO_3 Digestion	0.1	7.6	6.8	110%
Cr, HNO_3 Digestion	0.3	60.5	56.9	106%
Cr, H_2O_2/HNO_3 Digestion	0.2	59.9	56.9	105%

The participants were instructed to digest all samples according to Section 4.1.4 for "total recoverable metals." Hydrochloric acid is omitted for GFAAS analysis. A slight modification was made to the digestion procedure. Instead of filtering all samples at their reduced volume to remove precipitates as directed in the method, the analysts were instructed to redilute the samples back to their original volumes and filter only those that still contained precipitates. Some matrices have solids that may precipitate at the reduced volume but redissolve on dilution. This modification was noted in the instructions to the participants and also noted directly on the copy of the EPA Metals Method that was sent to each laboratory.

The AMQ-IV Round 2 study employed Youden paired samples (1) instead of replicate samples like those used in most of the previous AMQ studies. Results from replicate studies are sometimes considered suspect because of the potential for repeated analysis by analysts intent on obtaining results in close agreement. For this reason, the Youden pair study is preferred. A Youden pair consists of two closely matched samples of the same matrix with similar concentrations of the test element. Each sample is treated as a completely independent sample. This approach still allows for the calculation of intralaboratory precision statistics but removes the analyst's opportunity to bias the data.

2.3 Selection of Test Matrices

The AMQ-IV Round 2 matrices are shown in Table 2-3. Respondents to the survey discussed in Section 2.1 indicated a high level of interest in groundwater matrices. A low TDS groundwater from the midwest, acid mine drainage, and estuarine matrices were selected for this study. Reagent grade water matrix was selected to provide an estimate of the variability due to preparation and analysis when no significant interferents are present.

Table 2-3
Selected Test Matrices for AMQ-IV Round 2

Matrix	Reason for Selection
Midwest Groundwater	Low TDS groundwater sample with few interferents
Acid Mine Drainage (groundwater)	Complex matrix which has significant analysis problems
Estuarine	Major water source for coastal plants; complex matrix
Reagent Grade Water	Baseline matrix for comparison of stability and matrix effects

Members of the RP-1851 Project Advisory Committee provided the groundwater and estuarine matrices. Since the salinity of the estuarine sample varies seasonally, the salinity of the estuarine site was monitored weekly during the spring until the chloride content was at a relatively high level before the sample was collected. Prior to the preparation of validation samples, TRW determined the background concentration of each test element by ICP-MS using standard addition techniques. These values are included in the test concentration summaries presented in Section 2.4. For further matrix characterization, the background elements were determined by ICP-MS and the anion concentrations were measured by ion chromatography. Total dissolved solids and conductivity were also measured. The results of those analyses are found in Section 4.3.

In order to obtain sufficient data for the study, the participating laboratories were asked to analyze as many of the matrices as possible. All of the participants analyzed the midwest groundwater and reagent grade water samples. Most of the laboratories analyzed the estuarine and acid mine drainage samples.

2.4 Selection of Test Concentrations

The selection of test concentrations addressed the needs to:

- Challenge the analytical method at or near its detection limit.
- Stay within the published (EPA MCAW) estimate of the optimum analytical range if possible.
- Maximize the number of different test concentrations over the analytical range of each element.
- Overlap the intake and discharge spike concentrations for the freshwater and seawater matrices.
- Provide for dilution of the more complex matrices

ASTM recommends a minimum of three test levels (2). The AMQ-IV Round 2 program used four pairs of spiked samples plus a pair of unspiked background samples for each matrix, resulting in a total of ten samples per matrix.

The EPA (49FR 43430 Friday, October 26, 1984) has recommended an approach to calculating the Method Detection Limit (MDL). The analyte of interest is spiked into the matrix to obtain a concentration within a factor of 1 to 5 times the estimated limit of detection (1 to 10 times for reagent grade water.) Table 2-4 contains the detection limits estimated by the EPA (MCAW, EPA 600/4-79-020, Revised March 1983), the optimum range suggested by the EPA (MCAW), the non-cooling water discharge values obtained in Phase I of this project, and the Water Quality Criteria for the AMQ-IV Round 2 elements. Based on the data in Table 2-4, the initial spike concentrations for the freshwater (midwest groundwater) and reagent grade water, were targeted to satisfy the EPA requirements for the calculation of the MDL. The eighth and final spike concentration was at the upper limit of the optimum use range when background levels permitted. The spikes for the estuarine and acid mine drainage samples were a factor of 10 higher to permit dilution of these high dissolved solids matrices.

Tables 2-5 through 2-8 contain the total targeted concentrations for the AMQ-IV Round 2 validation effort based on the analysis of the unspiked samples. Prior to the test, each matrix was analyzed at TRW by ICP-MS to determine the background concentrations of the test elements. The amount of each element to be added to each matrix was calculated to reach the targeted concentrations. It should be noted that the true concentrations reported in Section 7 and the Appendix are computed from the mean value reported by the participants for the lowest concentrations. Tables 2-5 through 2-8 represent only TRW's estimate of the background and show the planned spike concentrations.

TRW conducted a series of tests to assess the compatibility of the three spiking solutions with each other and with the test matrices. A solution containing volumes of 1000 ppm single element ICP standards in the ration of 1:2:2 Cd:As:Cr was prepared and monitored. No evidence of precipitation was seen. Portions of this mixture were spiked into reagent grade water both immediately after preparation and 24 hours after preparation. The samples were then analyzed by ICP-MS. Recoveries were within ten percent of the spiked values. It was concluded that these standards could be combined in beakers for the short time necessary during the spiking activity without danger of precipitation of test elements.

Table 2-4
AMQ-IV Round 2 Background Information

Element	EPA GFAAS DL µg/L (1)	NCWD µg/L (2)	WQC µg/L (3)	EPA MCAW Optimum Range µg/L (1)
As	1	41	190	5-100
Cd	0.1	4.6	1.0	0.5-10
Cr	1	19	10 (hex)	5-100

(1) From EPA MCAW, Methods for Chemical Analysis of Water and Wastes, EPA 600/4-29/040, Revised March 1983

(2) Non-Cooling Water Discharge average concentration in Aggregate Ashpond Overflow (Source: EPRI CS-3741, November 1984)

(3) Freshwater Criteria Continuous Concentration expressed as dissolved (60 FR 22236, May 4, 1995), 100 mg/L hardness where applicable

Table 2-5
EPRI AMQ-IV Round 2 Target Spiked Concentrations for Reagent Grade Water

Element	EPA DL µg/L	Optimum Range µg/L	BKG	1	2	3	4	5	6	7	8
As	1	5-100	0	5	7	22	28	50	58	90	100
Cd	0.1	0.5-10	0	0.5	1.1	2.2	3.1	3.5	6	8.2	9.3
Cr	1	5-100	0	5	8	15	21	46	52	80	92

Table 2-6
EPRI AMQ-IV Round 2 Target Spiked Concentrations for Midwest Groundwater

Element	EPA DL µg/L	Optimum Range µg/L	BKG	1	2	3	4	5	6	7	8
As	1	5-100	0.8	5	9	18	23	40	48	86	92
Cd	0.1	0.5-10	<0.1	0.5	1.2	3.1	3.9	5.5	7	9	10
Cr	1	5-100	0.4	5	8	20	25	55	63	88	100

Table 2-7
EPRI AMQ-IV Round 2 Target Spiked Concentrations for Estuarine Water *

Element	EPA DL µg/L	Optimum Range µg/L	BKG	1	2	3	4	5	6	7	8
As	1	5-100	3.7	50	60	230	280	550	600	800	850
Cd	0.1	0.5-10	0.7	10	16	32	41	50	62	88	97
Cr	1	5-100	4	60	80	300	380	650	720	850	980

* Spiked to be within range when diluted 1:10

Table 2-8
EPRI AMQ-IV, Round 2 Target Spiked Concentrations for Acid Mine Drainage*

Element	EPA DL µg/L	Optimum Range µg/L	BKG	1	2	3	4	5	6	7	8
As	1	5-100	5.6	70	100	330	410	700	770	870	940
Cd	0.1	0.5-10	4	20	28	40	48	62	71	85	93
Cr	1	5-100	4	50	70	220	290	450	520	910	1000

* Spiked to be within range when diluted 1:10

To test for compatibility of the test elements with the study matrices, aliquots of the concentrated spiking solutions were spiked into samples of the matrices near the highest target spike concentrations and allowed to sit for approximately three weeks. The samples were then analyzed in duplicate by ICP-MS. No stability problems were noted. Tables 2-9 through 2-12 summarize the results of the stability testing.

Table 2-9
AMQ-IV Round 2 Pre-Test Stability of Concentrated Spiking Standards

Element	Spike	Bkg	Result 1	Result 2	Recovery
As	4000	0	4070	3950	100%
Cd	2000	0	1970	2000	99%
Cr	4000	0	4110	4120	103%

Table 2-10
AMQ-IV Round 2 Pre-Test Stability of Analytes in Midwest Groundwater

Element	Spike µg/L	Bkg µg/L	Result 1 µg/L	Result 2 µg/L	Recovery
As	90	0.8	94	95	104%
Cd	10	0	9.7	9.6	97%
Cr	80	0.4	82	81	101%

Table 2-11
AMQ-IV Round 2 Pre-Test Stability of Analytes in Acid Mine Drainage

Element	Spike µg/L	Bkg µg/L	Result 1 µg/L	Result 2 µg/L	Recovery
As	850	5.6	934	945	110%
Cd	90	4	97	95	102%
Cr	900	4.5	945	969	106%

Table 2-12
AMQ-IV Round 2 Pre-Test Stability of Analytes in Estuarine Water

Element	Spike µg/L	Bkg µg/L	Result 1 µg/L	Result 2 µg/L	Recovery
As	900	3.7	913	910	101%
Cd	80	0.7	79	78	97%
Cr	800	4	852	854	106%

2.5 References

1. W.J. Youden and E.H. Steiner, Statistical Manual of the Association of Official Analytical Chemists, 1975.

2. American Society for Testing and Materials, "Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water," D2777-96, *Annual Book of ASTM Standards*, 1997.

3

LABORATORY SELECTION FOR AMQ-IV ROUND 2

A comprehensive solicitation campaign consisting of phone calls to potential participants was conducted by TRW. A total of 26 laboratories was eventually enlisted for AMQ-IV Round 2, with 18 completing the analyses.

3.1 Solicitation Process

Starting with the list of participants culled from the AMQ-I, -II, -III and -IV Round 1 efforts, TRW initiated a telephone survey to determine whether the potential participants were interested in joining the AMQ-IV Round 2 effort and whether they had the requisite equipment.

3.2 Laboratory Selection Process

A key contact was identified and contacted by TRW personnel. A profile on the laboratory capabilities was developed using the Laboratory Contact Worksheet (Appendix B).

The following criteria were applied to the respondents:

- Experience with methods selected for qualification.
- Commitment/capability to do all or most of the AMQ-IV Round 2 elements.

After intensive solicitation effort, 26 laboratories were found to meet these criteria, 18 of which completed the study. Since few laboratories routinely analyze the elements of interest in acid mine drainage and estuarine samples, laboratories with experience analyzing complex matrices were solicited to analyze these samples. Table 3-1 lists the laboratories completing AMQ-IV Round 2. All participants analyzed the reagent grade water and midwest groundwater samples. Fifteen of the laboratories analyzed the estuarine samples and seventeen of the laboratories analyzed the acid mine drainage samples.

Table 3-1
Laboratories Completing AMQ-IV Round 2

	Matrices				**Elements**		
Laboratory	**GW**	**RGW**	**EST**	**AMD**	**As**	**Cd**	**Cr**
Alabama Power	X	X	X	X	X	X	X
BC Analytical - Glendale	X	X	X	X	X	X	X
CDS Laboratories	X	X	X	X	X	X	X
Centerior Services	X	X	X	X	X	X	X
Duke Power	X	X	X		X	X	
Duquesne Light	X	X	X	X	X	X	X
Florida Power	X	X	X	X	X	X	X
Kentucky Utilities Company	X	X	X	X	X	X	X
Micro Methods	X	X	X	X	X	X	X
New York State Electric & Gas Corporation	X	X	X	X	X	X	X
Pennsylvania Power & Light Company	X	X		X		X	X
Public Service Company of Colorado	X	X	X	X	X	X	X
San Diego Gas & Electric	X	X	X	X	X	X	X
Savannah Laboratories - Mobile, AL	X	X	X	X	X	X	X
South Carolina Gas & Electric Co.	X	X	X	X	X	X	X
Tampa Electric Company	X	X	X	X	X		X
Wisconsin Public Service Corp.	X	X		X	X	X	X
Wisconsin Electric Power Company	X	X		X	X	X	X

GW = Midwest Groundwater
RGW = Reagent Grade Water
EST = Estuarine
AMD = Acid Mine Drainage

4

AMQ-IV ROUND 2 SAMPLE PREPARATION AND DISBURSEMENT

The activities associated with sample preparation and disbursement included hardware checkout, sample acquisition, sample spiking, and development of participant instructions and reporting forms. Details of these activities are presented in the following sections.

4.1 Spiking Hardware Checkout and Equipment Calibration

AMQ-IV Round 2 employed the same churn splitters used in all of the AMQ studies. Figure 4-1 shows one of the four all-polyethylene 120-L churn splitters used in AMQ-IV Round 2. A separate churn splitter was used for each matrix to avoid cross contamination between the sample matrices.

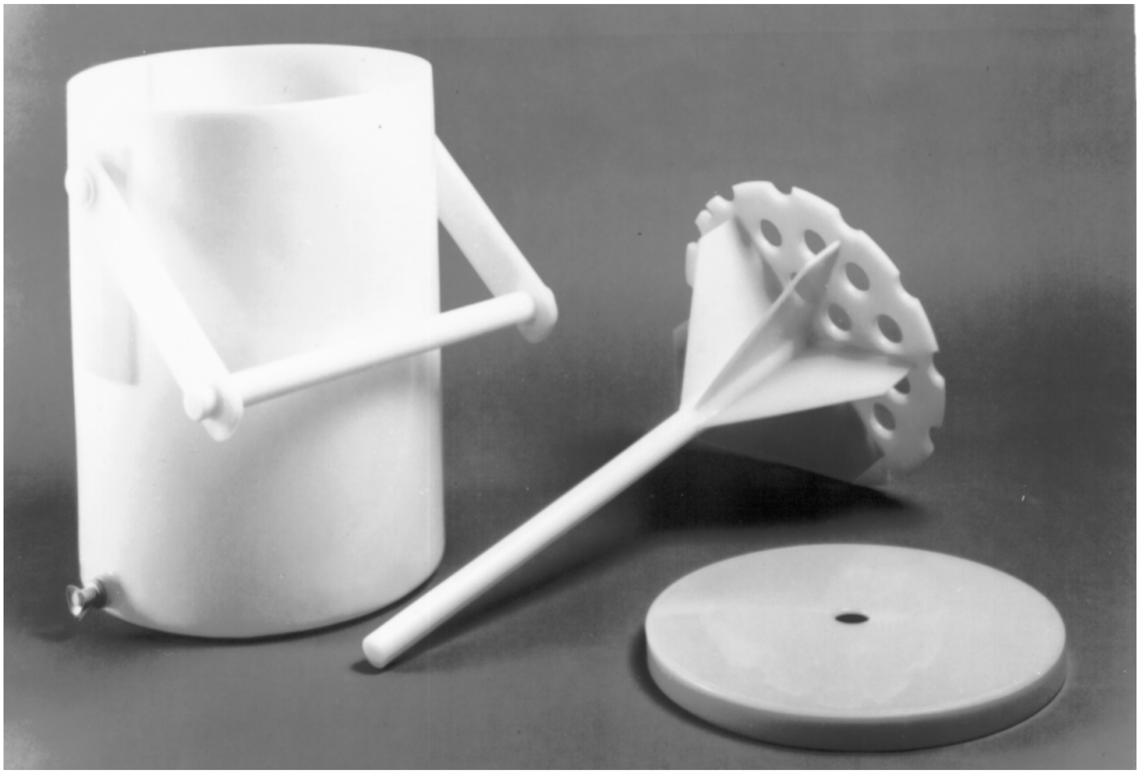


Figure 4-1 Photograph of Churn Splitter Used during AMQ-IV Round 2 Effort

As part of the AMQ-I study, a test was conducted to determine the time necessary for thorough sample mixing. After the churn splitter was filled with a known volume of deionized water, a manganese spiking solution was prepared so that thorough mixing with the water in the splitter would result in a manganese solution of exactly 5.0 ppm. After the spiking solution was added to the top layer of the water in the splitter, the churn handle was moved at a rate of 7 inches/second (18 cm/sec) and samples were withdrawn through the spigot at the bottom at specified time intervals. Manganese concentrations were determined by Flame AAS. The plot of manganese concentrations versus time (Figure 4-2) shows that top-to-bottom liquid movement was very rapid and that thorough mixing was achieved in less than three minutes. For the AMQ-IV Round 2 samples a five-minute mix period followed each spike addition.

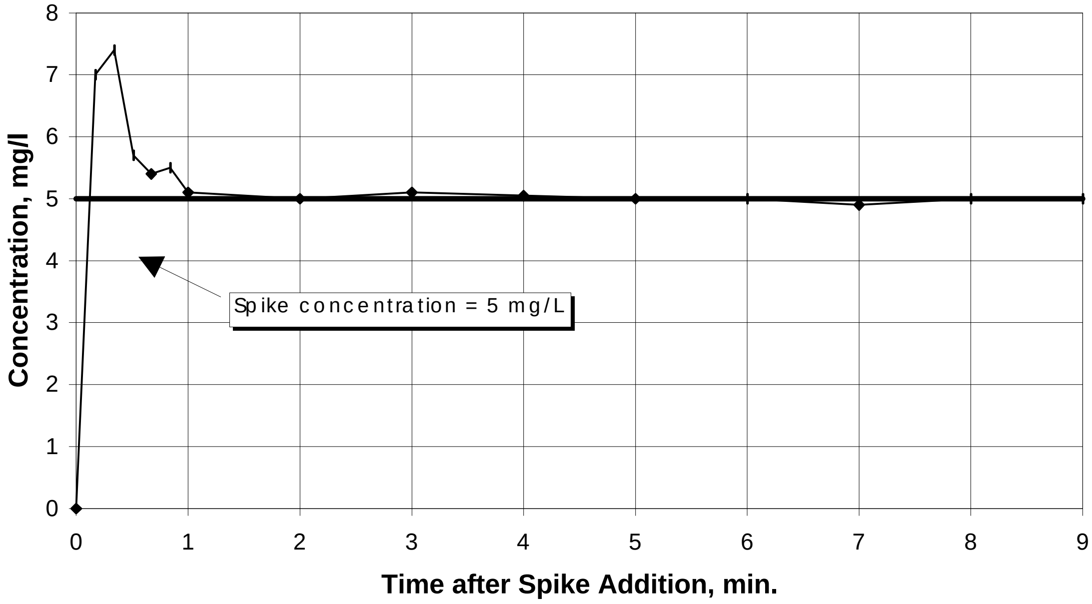


Figure 4-2 Plot of Manganese Concentrations with Time in the Churn Splitter

To calculate the amount of spiking solution required to prepare the test samples, the total solution volume in the churn splitter had to be known. A digital platform scale with 200 kg capacity was used to weigh the splitters and liquid contents to the nearest 0.05 kg. Whenever a volume measurement was needed, triplicate 50-mL aliquots of solutions were withdrawn for determination of solution density. The volume of solution in the churn splitter was then calculated from its weight and density. The scale was calibrated immediately prior to the spiking activity.

4.2 Sample Collection/Stabilization

Collection of the AMQ-IV Round 2 test matrices is described in the following sections. Since the AMQ program emphasized matrix effects rather than the absolute trace element concentrations of the matrices, no nitric acid was added to the field samples prior to their arrival at TRW. Upon receipt, and after aliquots were removed for pH, anion, and TDS analysis, samples were stabilized with Ultrex® grade nitric acid to pH<2. The amount of acid added and pH readings were recorded on an Acid Stabilization Worksheet (Figure 4-3). The stabilized samples were checked again in several hours and again on the day of spiking to verify that the pH remained below 2.

4.2.1 *Groundwater Sample Collection*

The midwest groundwater and acid mine drainage samples were collected by utility personnel at each utility's groundwater sampling site for the respective source. For each matrix, a total of 100 L was collected in four 25 L carboys. The carboys were cleaned by the procedure in Table 4-1 prior to shipment to the utility.

A complete set of sampling requirements and procedures was transmitted to the utility providing the samples prior to the collection. Approximately one gallon (4L) of sample was used to rinse each carboy and discarded. After rinsing, each container was filled with fresh sample to within two inches (5 cm) of the top and capped. Labels were then affixed with strapping tape. The filled carboys were repackaged in their original shipping crates and secured by padlocks. Federal Express 2-day service was used for transport to TRW.

4.2.2 *Estuarine Sample Collection*

A sample was collected weekly at the estuarine sampling site in order to monitor the arsenic, chromium and chloride concentrations. Once the concentrations of these analytes reached a level that the plant considered to be suitable, the matrix sample was collected. A total of 100 L of was collected in four 25 L carboys. The carboys were cleaned by the procedure in Table 4-1 prior to shipment to the utility.

Prior to the collection, a complete set of sampling requirements and procedures, the same as those for collecting the groundwater samples, was transmitted to the utility providing the samples.

ACID STABILIZATION OF AMQ SAMPLES

Matrix: ____________________

Date Stabilized: _____________

pH	Volume of Acid Added
1.	
2.	
3.	
4.	
5.	
6.	
7.	
8.	
9.	
10.	

Figure 4-3 Acid Stabilization Worksheet

Table 4-1
Method for Cleaning AMQ Sample Carboys, Disbursement Bottles and Churn Splitters

Step	Activity
1	Fill with 10% (w/w) HCl (AR grade).
2	Allow to stand 48 hours.
3	Empty and rinse with ASTM Type III water.
4	Fill with 10% (w/w) HNO_3 (AR grade).
5	Allow to stand 48 hours.
6	Empty and rinse with ASTM Type III water.
7	Fill with ASTM Type I water.
8	Allow to stand several weeks or until needed, changing water periodically to ensure continued cleaning.

4.3 Test Matrix Characterization

Once the samples were in-house, they were subjected to survey elemental and anion analyses to determine whether the sample concentrations roughly fit the concentration needs of the project and to characterize the background chemical composition of the samples.

Samples for anion, conductivity and total dissolved solids (TDS) analyses were withdrawn and stored under refrigeration prior to stabilizing the matrices with nitric acid. Duplicate samples of the stabilized matrices were analyzed by Inductively Coupled Plasma - Mass Spectrometry to characterize the major constituents of the test matrices. These results are contained in Table 4-2.

The three AMQ-IV Round 2 analytes are listed first in the table, followed by other cations of interest. The background cation data along with the anion, conductivity and TDS results yield important information on the chemical make-up of the matrices. These samples were deemed suitable for the study's needs.

Participants were told that the high TDS matrices, estuarine and acid mine drainage, had high concentrations of dissolved solids. It was recommended that they dilute these samples and the matrix spikes were selected accordingly. Most of the participants diluted these samples by a factor of ten.

Table 4-2
Background Data for AMQ-IV Round 2 Test Matrices
(Results in mg/L unless otherwise noted.)

Analyte	Groundwater	Estuarine	Acid Mine Drainage
As (µg/L)	0.8	3.7	5.6
Cd (µg/L)	nd<0.1	0.7	4.0
Cr (µg/L)	0.4	4.0	4.0
Ag	nd<0.004	nd<0.004	nd<0.004
Al	0.02	0.18	51
B	0.02	0.40	0.27
Ba	0.080	0.053	0.026
Be	nd<0.01	nd<0.01	0.01
Ca	81	45	120
Co	nd<0.002	0.003	0.44
Cu	nd<0.003	0.004	0.021
Fe	0.1	0.5	652
K	1.5	55	5.9
Mg	38	130	45
Mn	0.004	0.066	17
Mo	nd<0.008	0.021	nd<0.008
Na	5.1	1085	39.9
Ni	nd<0.003	0.004	0.84

Table 4-2
Background Data for AMQ-IV Round 2 Test Matrices
(Results in mg/L unless otherwise noted.)

Analyte	Groundwater	Estuarine	Acid Mine Drainage
Pb	nd<0.002	0.048	0.007
Se	nd<0.05	nd<0.05	nd<0.05
Sn	nd<0.003	0.056	nd<0.003
Sr	14	0.85	0.55
Ti	nd<0.006	nd<0.006	nd<0.006
V	nd<0.003	nd<0.003	0.025
Zn	nd<0.008	0.011	1.7
Zr	nd<0.003	nd<0.003	nd<0.003
Fluoride	<1	<1	<1
Chloride	5	1750	25
Bromide	<1	8	<1
Nitrate	<1	<1	<1
Sulfate	65	265	1900
Phosphate	<1	<1	<1
TDS	400	3800	3000
Conductivity, µmhos/cm	530	5700	2500

4.4 Procedures For Sample Processing

Bottle identity was tracked by using a two-step process to separate the filling and sorting/packing steps. As a result, the number of different ongoing activities during the filling operation was minimized. This two-step process ensured bottle identity by:

- Using a two-label system as a cross check

- Having only bottles for one matrix and one spike concentration level off the storage shelf at one time

The accuracy of spike additions was controlled by:

- Use of a Spike Calculation Worksheet discussed in Section 4.4.2
- Operation of the churn handle at pre-calibrated rates to ensure complete mixing

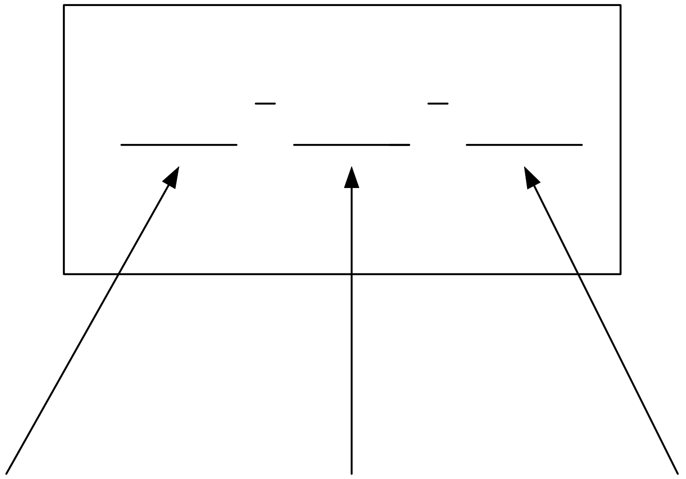
4.4.1 *Sample Tracking System*

Two sets of sample labels were used. The Pre-test Labels were placed on the bottles directly before the spiking/splitting activity began. These labels were used to identify matrix, spike concentration level, and filling order and eliminated the need for any hand-labeling during the labor-intensive spiking/splitting activity. Figure 4-4 contains the Pre-test Label coding. After filling, the bottles for each spike concentration level were stored on a separate shelf until preparation of individual laboratory packages. The adhesive backed final Test Labels were affixed during the packaging of samples for shipment, thus providing a double check of sample identity and reducing the chance of sample confusion.

The Test Label contains the following information:

- Laboratory Identification Number
- Matrix Identification Code
- Spiking Concentration Level
- Bottle Filling Order

With the exception of the bottle filling order, all other identifiers were entered on the Test Label prior to sample preparation. The filling order number from the Pre-test Label was entered into the last two digits of the sample identification number on the Test Label which was affixed to the bottle. For AMQ-IV Round 2, a Youden paired study, the spiking level was not revealed to the analysts. Instead, the spike level was indicated by a code letter on the Test Label. Figure 4-5 shows the blank final Test Label. The actual sequence of events during sample preparation and processing is discussed in the following sections.



Matrix

FW
AMD
EST
RGW

Spiking Concentration Level

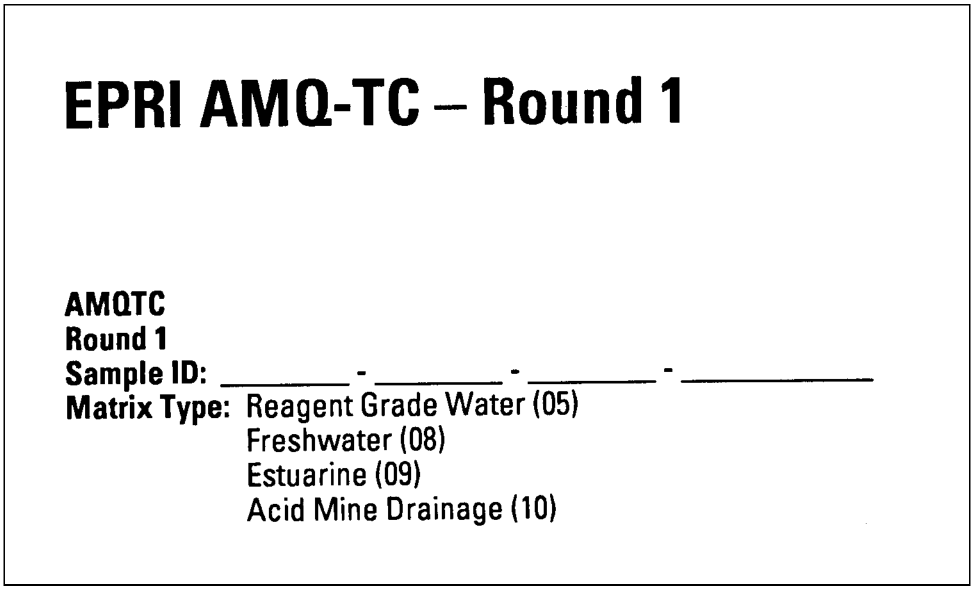
BKG = No Spike
01 = First Spike
02 = Second Spike
03 = Third Spike
04 = Fourth Spike
05 = Fifth Spike
06 = Sixth Spike
07 = Seventh Spike
08 = Eighth Spike

Filling Order

(1 to 99)

FW: Midwest Groundwater (Fresh)
AMD: Acid Mine Drainage
EST: Estuarine
RGW: Reagent Grade Water

Figure 4-4 Pre-Test Label Coding



EPRI AMQ-TC – Round 1

AMQTC
Round 1
Sample ID: ________ - ________ - ________ - ____________
Matrix Type: Reagent Grade Water (05)
Freshwater (08)
Estuarine (09)
Acid Mine Drainage (10)

Figure 4-5 Test Label for Sample Bottles

4.4.2 *Sample Filling Procedure*

Figure 4-6 provides an overview of the filling procedure. The stepwise procedure follows:

a. Place the empty churn splitter on the scale and record its tare weight on the Spike Calculation Worksheet (Figure 4-7).

b. Empty the carboys for the current matrix into the designated churn splitter. Churn for 5 minutes to mix.

c. Measure pH and record on the pH Verification Worksheet (Figure 4-8). Adjust pH, if necessary, to <2 by adding 5 mL increments of concentrated nitric acid (Ultrex grade, Baker Chemical).

   — Operate churn handle for 5 minutes. Check pH and adjust as needed with the acid. Record all data on the Pre-Spike pH verification Worksheet.

   — Repeat until pH is reduced to <2.

   — Operate churn handle for 30 minutes in "5 minutes on/5 minutes off" cycle. Check the pH every ten minutes. If the pH remains stable at <2, then record the pH on the pH Verification Worksheet. If the pH>2, repeat step c.

d. Fill a tared 50 mL volumetric flask with sample. Weigh the filled flask and calculate the density by using the formula:

$$Density = \frac{Weight\ of\ 50\ mL\ of\ Sample\ in\ Grams}{50\ mL} \qquad \text{(eq. 1)}$$

Perform in triplicate. Record all weights on the density determination portion of the pH Verification Worksheet.

e. Move the bottles for the background portion of the current matrix to the bench top adjacent to the churn splitter.

f. Place the Pre-Test Labels on the bottles.

g. Empty the Type I Water from these bottles one at a time. Inspect the bottle for residual DI water. If no residual water is observed, fill the bottle as indicated in Step h. If residual water is observed, rinse the bottle with a small portion (approximately 25 mL) of the current spike concentration level sample from the churn splitter. Dump the rinse into a waste container and inspect the bottle. If a film is still found, discard the bottle. All bottles passing this inspection are filled as indicated in Step h.

h. Operate the churn handle at 7 inches/second (18 cm/sec) for five minutes. While continuing to operate the handle, fill the bottles for the current spike level. Replace the top and wipe the outside of the bottle dry. Place the bottle on the designated shelf.

i. After all sample bottles have been filled for a given spike concentration, record the weight of the churn splitter and sample solution on the Spike Calculation Worksheet. Calculate the spike requirements for each element.

j. Weigh the precleaned Teflon beaker for this spike and record the values on the Spike Calculation Worksheet. The total beaker weights in the churn at the end of each spike will be added to the tare weight on the next higher spike.

k. Using the required single element standards (Inorganic Ventures, certified), weigh out the first standard into a polystyrene disposable beaker. Transfer the solution quantitatively into a precleaned Teflon beaker. Repeat with the remaining two standards.

   Place the Teflon beaker containing the standards on the churn paddle and tip the beaker over to empty the spiking solutions into the sample. Churn for 5 minutes at 7 inches/sec (18 cm/sec).

l. Move the bottles for the current spike concentration level to the bench top adjacent to the churn splitter.

m. Repeat steps f through l until all of the spike concentration levels have been completed.

n. Repeat steps a through m for each subsequent matrix.

At the end of the filling effort, all sample bottles carried a Pre-Test Label and were segregated in a cabinet by matrix and spike concentration level. The next step was to package the appropriate bottles and forms into boxes for shipment to each laboratory.

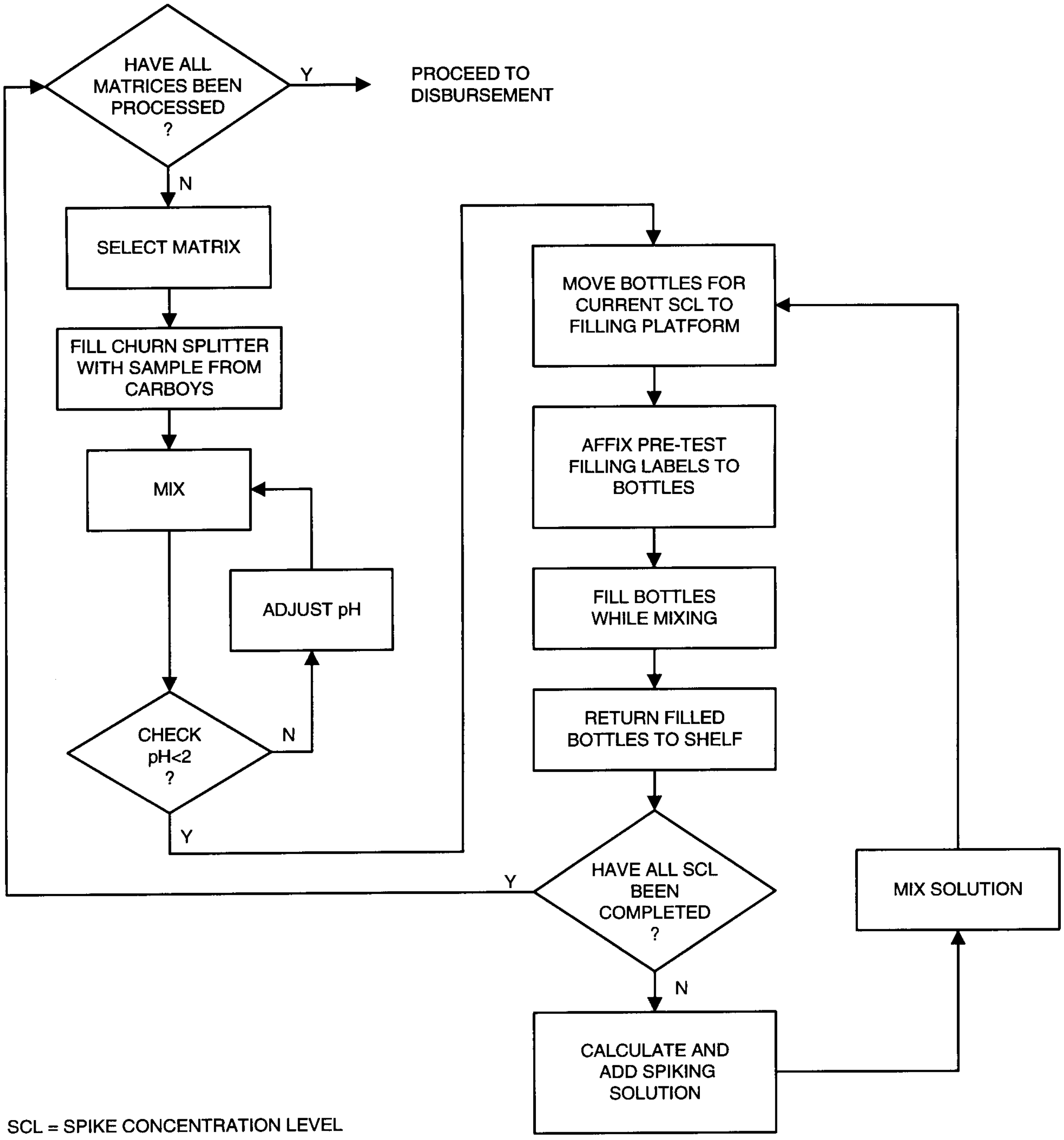
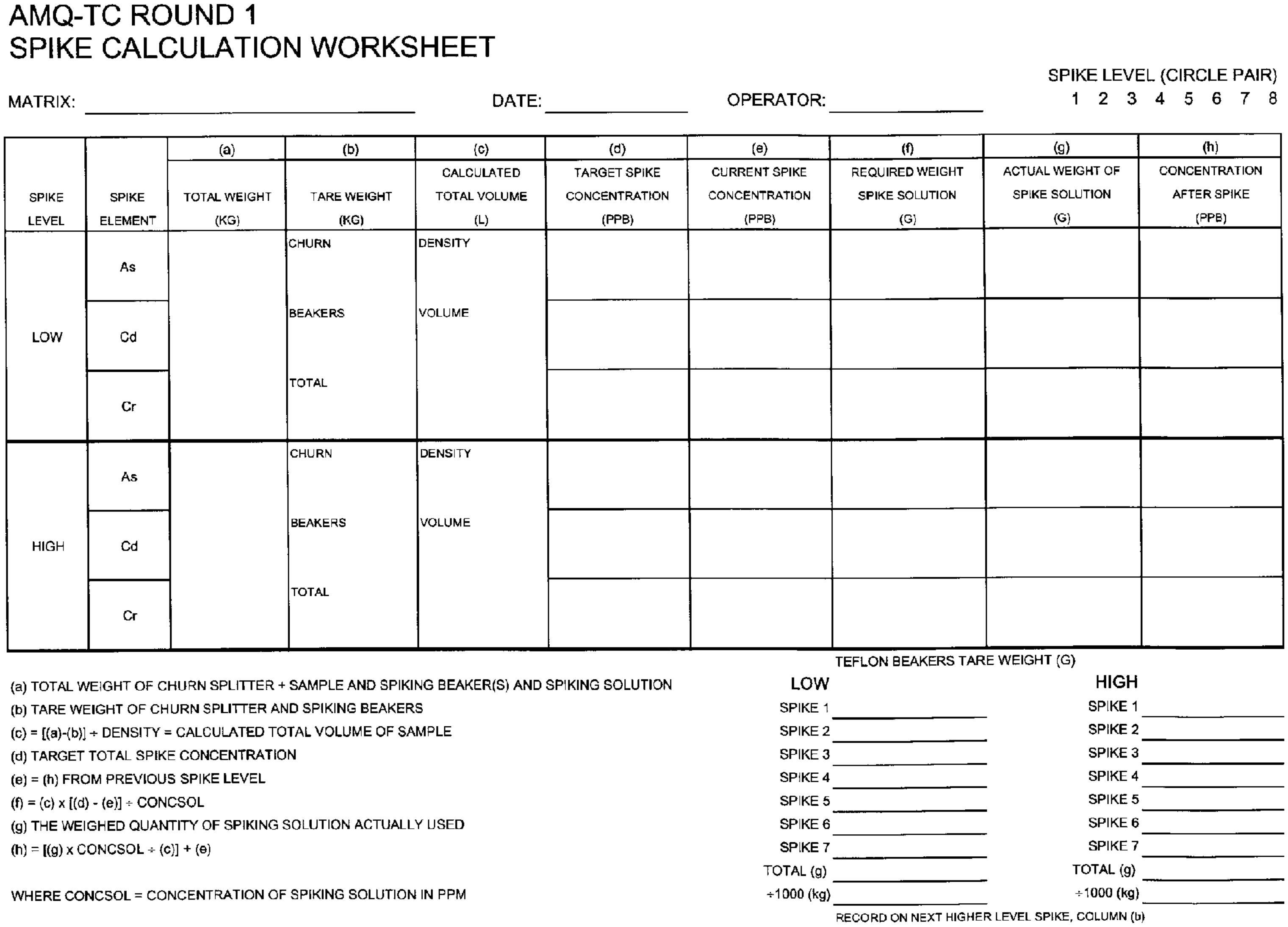


Figure 4-6 Bottle Filling Procedure



AMQ-TC ROUND 1
SPIKE CALCULATION WORKSHEET

MATRIX: ______________ DATE: ______________ OPERATOR: ______________

SPIKE LEVEL (CIRCLE PAIR)
1 2 3 4 5 6 7 8

		(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)
SPIKE LEVEL	SPIKE ELEMENT	TOTAL WEIGHT (KG)	TARE WEIGHT (KG)	CALCULATED TOTAL VOLUME (L)	TARGET SPIKE CONCENTRATION (PPB)	CURRENT SPIKE CONCENTRATION (PPB)	REQUIRED WEIGHT SPIKE SOLUTION (G)	ACTUAL WEIGHT OF SPIKE SOLUTION (G)	CONCENTRATION AFTER SPIKE (PPB)
LOW	As		CHURN	DENSITY					
	Cd		BEAKERS	VOLUME					
	Cr		TOTAL						
HIGH	As		CHURN	DENSITY					
	Cd		BEAKERS	VOLUME					
	Cr		TOTAL						

(a) TOTAL WEIGHT OF CHURN SPLITTER + SAMPLE AND SPIKING BEAKER(S) AND SPIKING SOLUTION
(b) TARE WEIGHT OF CHURN SPLITTER AND SPIKING BEAKERS
(c) = [(a)-(b)] ÷ DENSITY = CALCULATED TOTAL VOLUME OF SAMPLE
(d) TARGET TOTAL SPIKE CONCENTRATION
(e) = (h) FROM PREVIOUS SPIKE LEVEL
(f) = (c) x [(d) - (e)] ÷ CONCSOL
(g) THE WEIGHED QUANTITY OF SPIKING SOLUTION ACTUALLY USED
(h) = [(g) x CONCSOL ÷ (c)] + (e)

WHERE CONCSOL = CONCENTRATION OF SPIKING SOLUTION IN PPM

TEFLON BEAKERS TARE WEIGHT (G)

LOW		HIGH	
SPIKE 1		SPIKE 1	
SPIKE 2		SPIKE 2	
SPIKE 3		SPIKE 3	
SPIKE 4		SPIKE 4	
SPIKE 5		SPIKE 5	
SPIKE 6		SPIKE 6	
SPIKE 7		SPIKE 7	
TOTAL (g)		TOTAL (g)	
÷1000 (kg)		÷1000 (kg)	

RECORD ON NEXT HIGHER LEVEL SPIKE, COLUMN (b)

Figure 4-7 Spike Calculation Worksheet AMQ-IV Round 2

AMQ-IV Round 2

Pre-Spike pH Verification
and
Density Determination

pH Verification

pH Reading	Estimated Acid Required to Achieve pH	Acid Added	
		Volume	Time Mixed
1.			
2.			
3.			
4.			

Acid Lot No. ___________________

Density Determination

	1		2		3	
						Gross Weight, g Sample + Flask
-		-		-		Tare Weight, g Flask
						Net Weight, g Sample
÷	50	÷	50	÷	50	Divide by Flask Volume, mL
						Density, g/mL

Figure 4-8 pH Verification Worksheet

4.4.3 *Packaging Samples for Disbursement to Participating Laboratories*

An overview of the steps that comprise the packaging operation is presented in Figure 4-9 and details of these activities are presented in the following sections. In general:

- Filling order numbers are entered on each of three matching Identification (ID) Labels.
- Identical ID Labels are placed on a Test Label, Laboratory Data Reporting Form (LDRF) and Distribution Record.
- Test Labels are placed on the bottles.
- The sample bottles are sealed in polyethylene bags and placed in shipping cartons.
- The accompanying paperwork is placed in a large envelope in the carton.

In order to eliminate the labor intensive step of typing all of the sample Test Labels, a system employing computer generated adhesive Identification (ID) Labels was devised. The ID Labels were prepared in sets of three, containing all the information required for the Test Label except the bottle filling order. This was entered during packaging. Sets of ID Labels were prepared in the order they were to be placed on the bottles. The spiking order was identified by a letter code in order to disguise the relative spiking level. After entering the bottle filling order on each of the three ID Labels, one was placed on the Test Label, one on the LDRF and one on the Distribution Record. This accomplished the following:

- The bottle was fully identified for distribution to the participant.
- The LDRF sample ID exactly matched the bottle label.
- A record was maintained of each bottle sent to each participant.

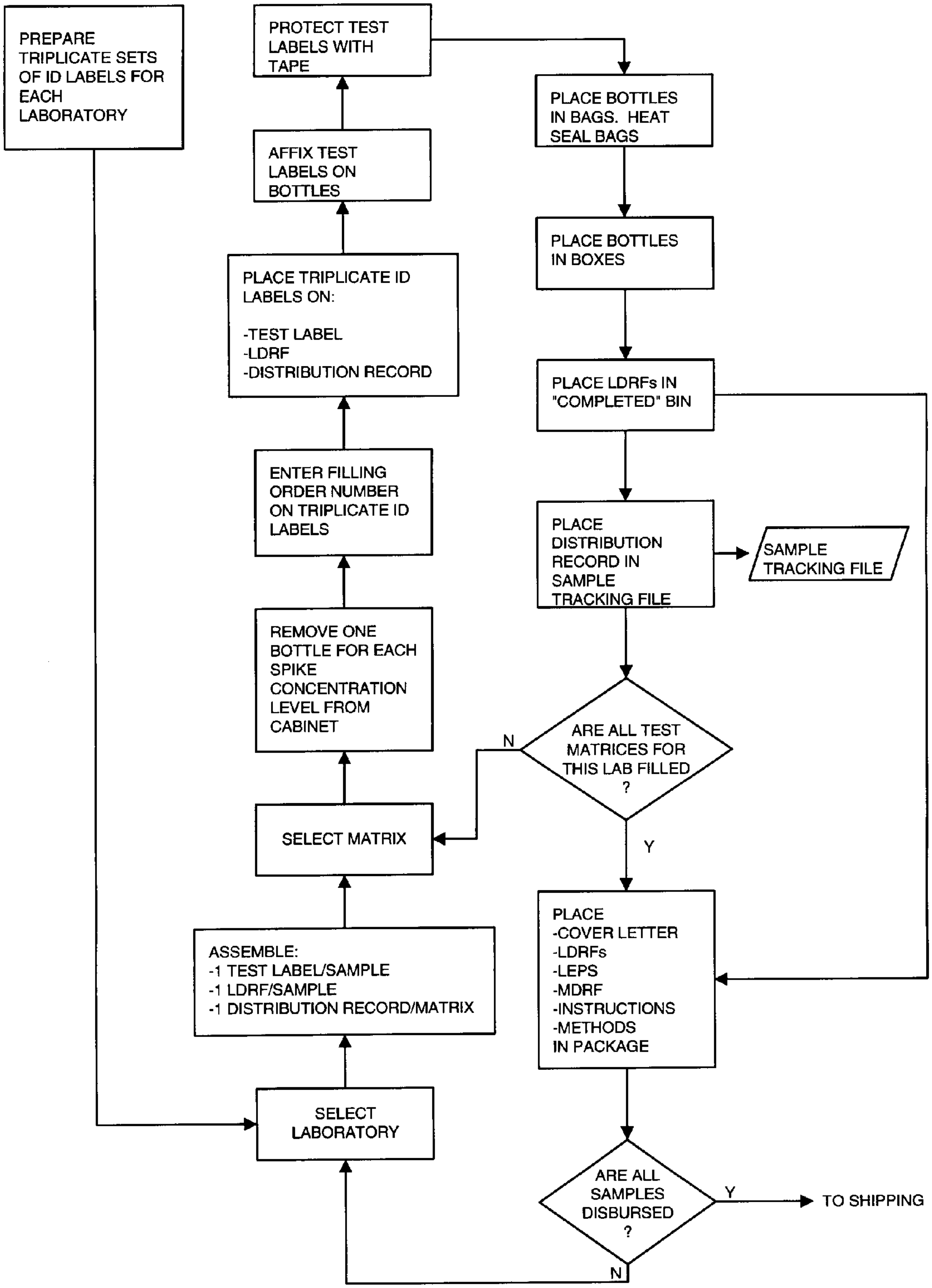


Figure 4-9 Sample Packaging Procedure

The following describes the packaging procedure:

a. A laboratory is selected and the required number of blank forms are assembled for that laboratory:
   - Test Labels - one for each sample.
   - Lab Data Reporting Forms (LDRFs) - one for each sample.
   - Distribution Records - one for each matrix.

b. The Spiking Level Code sheet, which translates the spiking level number on the Pre-Test Label to the spiking level letter code on the Identification Labels is placed in a prominent position for easy reference.

c. The prepared Identification (ID) Labels are assembled in the order used (lowest to highest) for the selected laboratory and matrix. The Spiking Level Code Sheet is used to verify that the labels were in the correct order.

d. A bottle with the first spike concentration level of the same matrix selected in Step c is removed from the shelf.

e. A bottle with the next highest spike concentration level of the same matrix selected in Step b is removed from the shelf.

f. Step e is repeated until all of the spike concentration levels for a given matrix have been assembled. The bottles are lined up in the sample processing area in ascending order of spiking level.

g. The bottle with the lowest spiking level is selected.

h. The Spiking Level Code Sheet is used to select the correct set of three ID Labels for the selected bottle.

i. The bottle filling order on the Pre-Test Label is entered on each of the three ID Labels.

j. After checking the three ID labels to verify that they are identical, one is placed on the Test Label, one on the LDRF and one on the Distribution Record.

k. After double checking the Spiking Level Code Sheet to verify that the letter code is correct for the spiking level, the Test Label is placed on the bottle completely covering the Pre-Test Label.

l. The bottle label is secured with wide transparent tape, the sample bottle is placed in a polyethylene bag, the bag is heat sealed and the sample is placed in the shipping carton. The completed LDRFs are placed in the "completed" bin.

m. Steps g through l are repeated until all bottles for the selected matrix have been processed.

n. Steps c through m are repeated with the remaining matrices for the selected laboratory.

o. All of the forms for a given laboratory are collated: the cover letter, the "Instructions to the Laboratories," "Laboratory Data Reporting Forms," "Laboratory Equipment and Practices Survey," "Method Parameters Reporting Form," and the specific analytical methods to be employed. They are then placed in a large envelope, which is shipped inside the carton. Finally, the carton is sealed and the shipping label is secured to the carton.

p. Steps a through o are then repeated for the remainder of the laboratories.

In this instance, the analytical methods included were the EPA Metals Method (Atomic Absorption), and EPA Methods 206.2, 213.2 and 218.2.

4.4.4 *Shipping of Samples to the Participating Laboratories*

The processed samples were shipped to the participating laboratories via two-day air express. Although the processed samples contained nitric acid, the acid concentration was below the 0.15% (wt/wt) nitric acid corrosive criterion established by the U.S. Department of Transportation in 49 CFR Part 173.

4.5 Instructions To Participating Laboratories

The instructions to participating laboratories provided information on:

- Elements and matrices to be tested
- Bottle coding
- Reporting requirements
- Preparation and analytical procedures

Appendices C through F contain a copy of the instructions, Laboratory Data Reporting Form (LDRF), Laboratory Equipment and Practices Survey (LEPS), and Method Parameters Reporting Form (MPRF) which were sent to the participating laboratories. Annotated copies of the EPA MCAW Metals Method, Method 213.2 for cadmium, Method 206.2 for arsenic and Method 218.2 for chromium were also sent to all the participants. The LEPS is designed to collate information on the equipment and laboratory practices used by the participant during sample analysis. It also asks some basic questions concerning analyst and supervisor experience and education. The MPRF solicits information on the instrument operating parameters used to analyze the samples. The data obtained from the LEPS and MPRF are discussed in Section 7. A LDRF was included for each sample. Analysts were instructed to report all analytical results, including zero and negative values, on the LDRFs.

5

QUALITY ASSURANCE/QUALITY CONTROL

Detailed procedures were prepared for the spiking, filling and shipment of samples as described in the preceding section. Besides carefully following those procedures, TRW implemented the following quality assurance measures during disbursement:

- The spiking and disbursement activity was audited by TRW personnel experienced in contamination control. Adherence to the test plan was closely monitored.
- Special single element standards made from "6 nine's" metal or primary standards were used for all spike solutions.
- Separate churn splitters were used for each matrix.
- The spiking laboratory was cleaned floor to ceiling prior to the sample spiking operation and was made off limits to all but the AMQ disbursement personnel.
- Sample concentrations were verified by analyzing the sample bottles containing the highest test concentration.
- Prior to shipment, filled sample bottles were stored in locked cabinets. Labeling protocol provided traceability with regard to order of filling.

Approximately three months after the samples were shipped to the participants, samples retained at TRW were analyzed to confirm sample stability. The EPA permits nitric acid stabilized samples to be stored for up to six months prior to the determination of most trace metals. It was decided that, since the participating laboratories would analyze the samples anywhere from one to two months after they were bottled, the stability of the samples should be confirmed. During the test round, duplicate samples from the lowest and highest test concentration bottles from each matrix were analyzed for the test elements approximately three months after filling. The spike recovery was computed and compared to the amount actually added to the test samples.

The results of the verification and stability check analyses are described in the following sections.

5.1 Analyses to Verify AMQ-IV Round 2 Sample Concentrations

During the AMQ-IV Round 2 test program, verification of the test concentrations was accomplished by indirect and direct methods. The indirect methods included auditing the spiking procedure, calibrating the scale used to weigh the churn splitter, and auditing the spike log books. Besides these indirect practices, the highest test concentration sample from each matrix was analyzed for each element before the samples were disbursed to the participants. If an error occurred in any one of the spiking steps, it would show up in the highest test concentration. The results of these analyses are found in Table 5-1 and Figures 5-1 through 5-3. The samples were analyzed by TRW personnel using Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). These analyses did not indicate any significant differences between the calculated and measured concentrations. All measured element concentrations were within +/-10 % of the calculated values. All of the test elements were within the analytical precision expected at the test concentrations.

5.2 Analyses to Confirm Stability in AMQ-IV Round 2

The highest and lowest concentration test samples from each matrix were analyzed for the three test elements approximately three months after spiking. Analyses were performed in duplicate by TRW using ICP-MS. Figures 5-1 through 5-3 summarize the results of the stability analyses for the highest concentration samples. The actual analysis data are found in Table 5-1. Recoveries were calculated by ratioing the difference between the measured concentration of the highest and lowest samples for a given matrix to the added spike. The recoveries ranged from a low of 99% (arsenic in estuarine) to a high of 108% (chromium in reagent grade water). The results confirmed that there had been little or no change in the test samples with time.

Table 5-1
Summary of Verification and Stability Analyses for AMQ-IV Round 2

	Arsenic			Cadmium			Chromium		
Matrix	**CV µg/L**	**Verify µg/L**	**Stability µg/L**	**CV µg/L**	**Verify µg/L**	**Stability µg/L**	**CV µg/L**	**Verify µg/L**	**Stability µg/L**
RGW-1	5.0	-----	4.9	0.5	-----	0.6	5.2	-----	5.3
RGW-8	100	100	106	9.5	9.6	10.0	91.1	97.3	98.5
Recovery		100%	106%		101%	104%		107%	108%
FW-1	5.0	-----	5.0	0.4	-----	0.5	5.2	-----	4.6
FW-8	91.9	92.2	93.0	10.4	10.0	10.5	100	102	102
Recovery		100%	101%		96%	100%		102%	103%
AMD-1	69.4	-----	72.3	20	-----	20.1	49.9	-----	51.2
AMD-8	941	970	968	93.3	92.4	94.5	999	1045	1000
Recovery		103%	103%		99%	102%		105%	100%
EST-1	48.6	-----	54.0	9.9	-----	9.5	60.1	-----	58.1
EST-8	857	836	854	97.6	94.0	97.5	957	985	980
Recovery		98%	99%		96%	100%		103%	103%

RGW = Reagent Grade Water
AMD = Acid Mine Drainage
FW = Midwest Groundwater (freshwater)
EST = Estuarine
CV = Calculated Value. Based on original TRW background analysis plus added spikes.
Verify = Results of TRW verification analysis of highest concentration samples prior to shipment.
Stability = Results of TRW stability analysis 3 months after sample preparation.
Recovery: Verify = Ratio of measured concentration to CV
Recovery: Stability = Ratio of difference between the measured concentrations of highest and lowest samples from the stability analysis to the CV

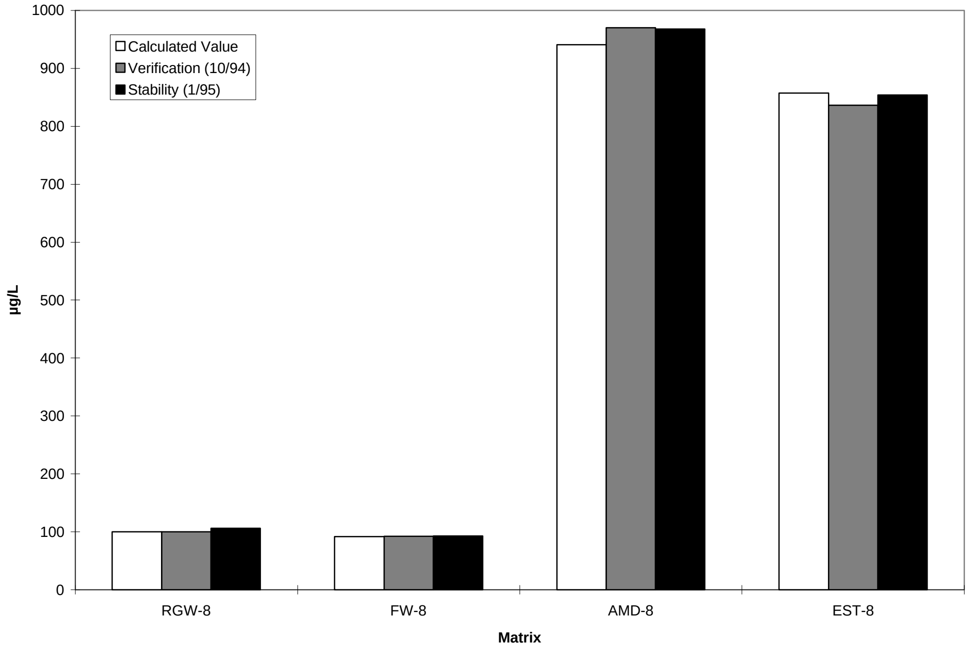


Figure 5-1 QA/QC Analysis of Highest Concentration Samples for As

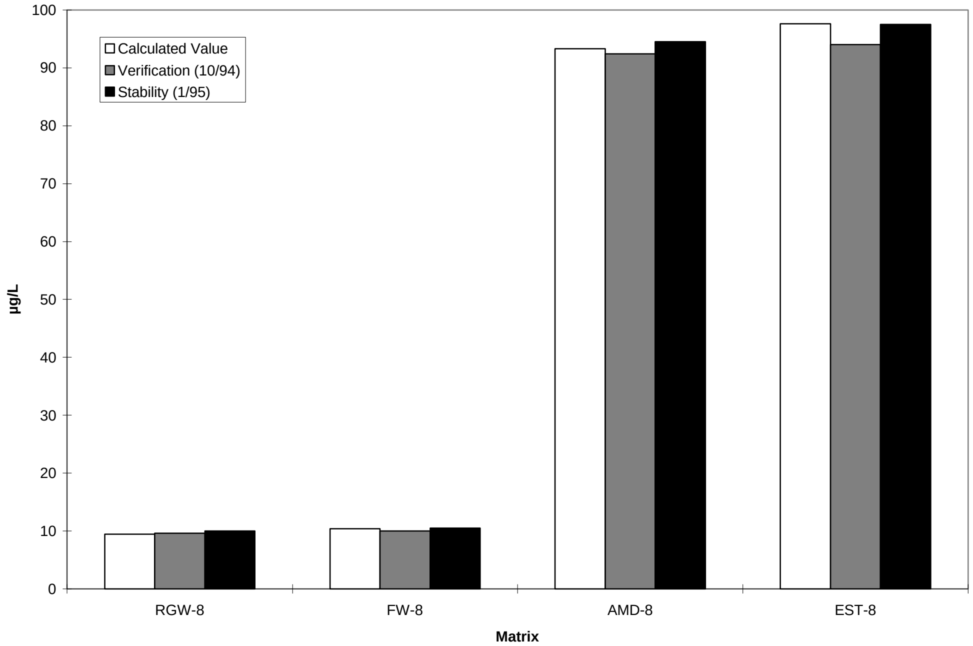


Figure 5-2 QA/QC Analysis of Highest Concentration Samples for Cd

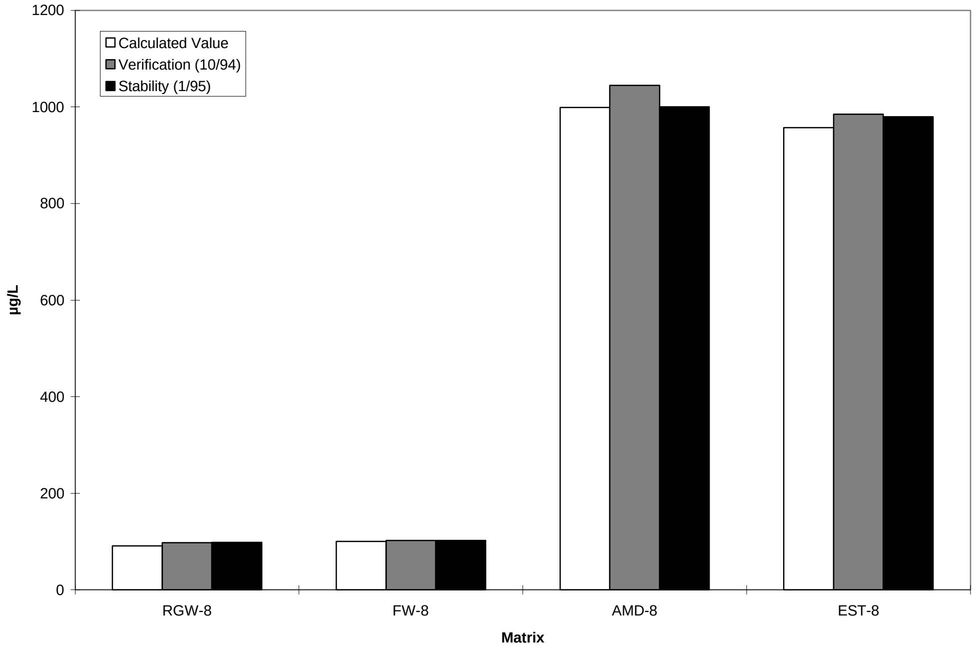


Figure 5-3 QA/QC Analysis of Highest Concentration Samples for Cr

6

AMQ STATISTICAL ANALYSIS PROGRAM

Data for this method performance study were analyzed by STATCALC, a data preparation and statistical analysis program developed by EPRI which provides computer processing according to the ASTM D2777 method. Figures 6-1, 6-2 and 6-3 provide an overview of the program.

6.1 STATCALC Collaborative Statistical Analysis Program

STATCALC is a set of software programs designed to operate in the personal or desktop computer environment, commonly known as an “IBM-PC”. STATCALC was designed to analyze data resulting from collaborative analytical method validation studies. Such studies are conducted, both by government regulatory bodies and by private industry, to assess the precision and bias of analytical methods. The program uses procedures based on and developed using sound scientific principles, procedures that have been demonstrated and verified with actual field studies.

STATCALC was conceived and developed as a computer-assisted implementation of the preparatory and statistical information processing required by a well-known and successful standard for collaborative laboratory studies, ASTM D2777-86 (1). This standard, while very detailed with examples for collaborative studies with replicate experimental design, also provides for the studies based upon Youden pairs. The experimental design for this method performance study uses the processing subprogram "YOUDENPR", which has a capacity of 100 laboratories with five Youden pair observations per laboratory for each analyte and matrix.

Over the course of the AMQ study, the STATCALC program was modified to conform to the latest version of ASTM D2777. The version used to reduce the data for the AMQ-IV Round 2 study was compliant with ASTM D2777-96 (2).

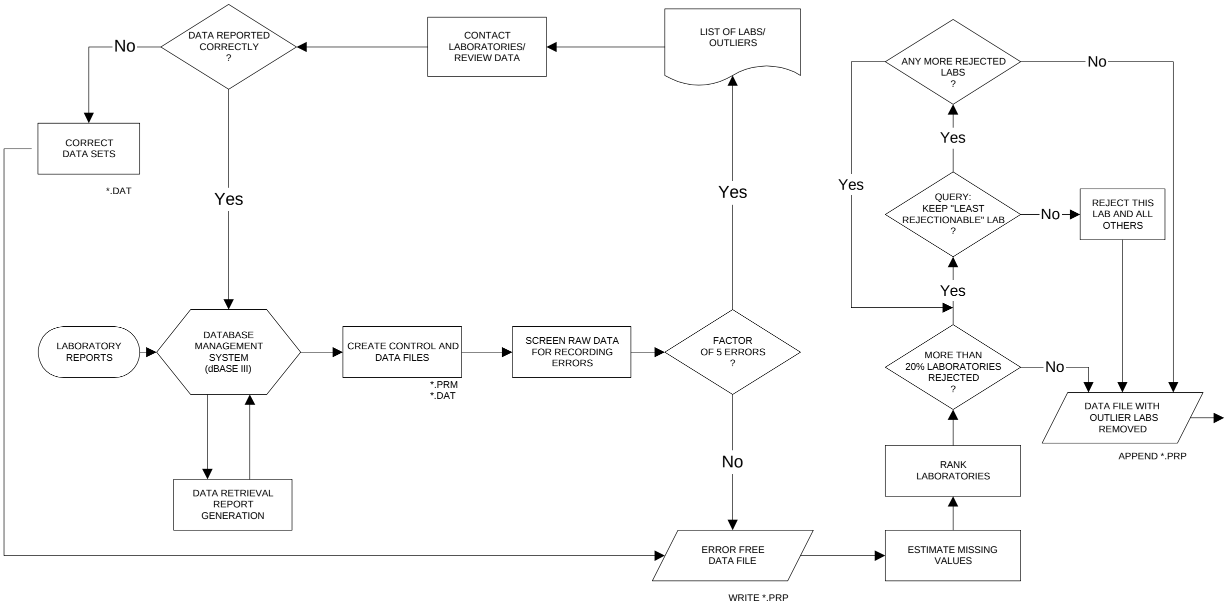


Figure 6-1 STATCALC Data Screening/Lab Ranking

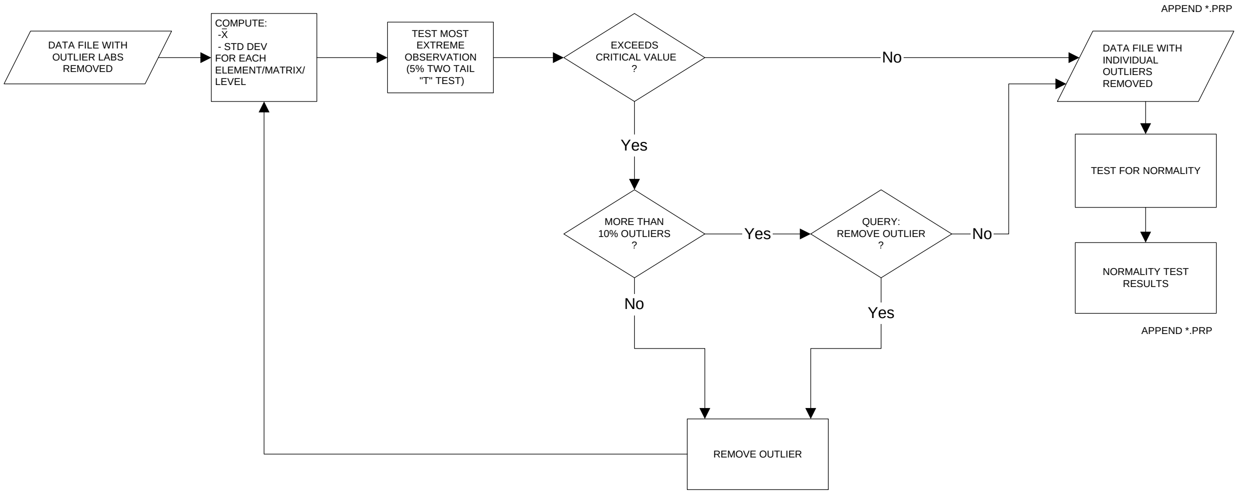


Figure 6-2 STATCALC Outlier Testing

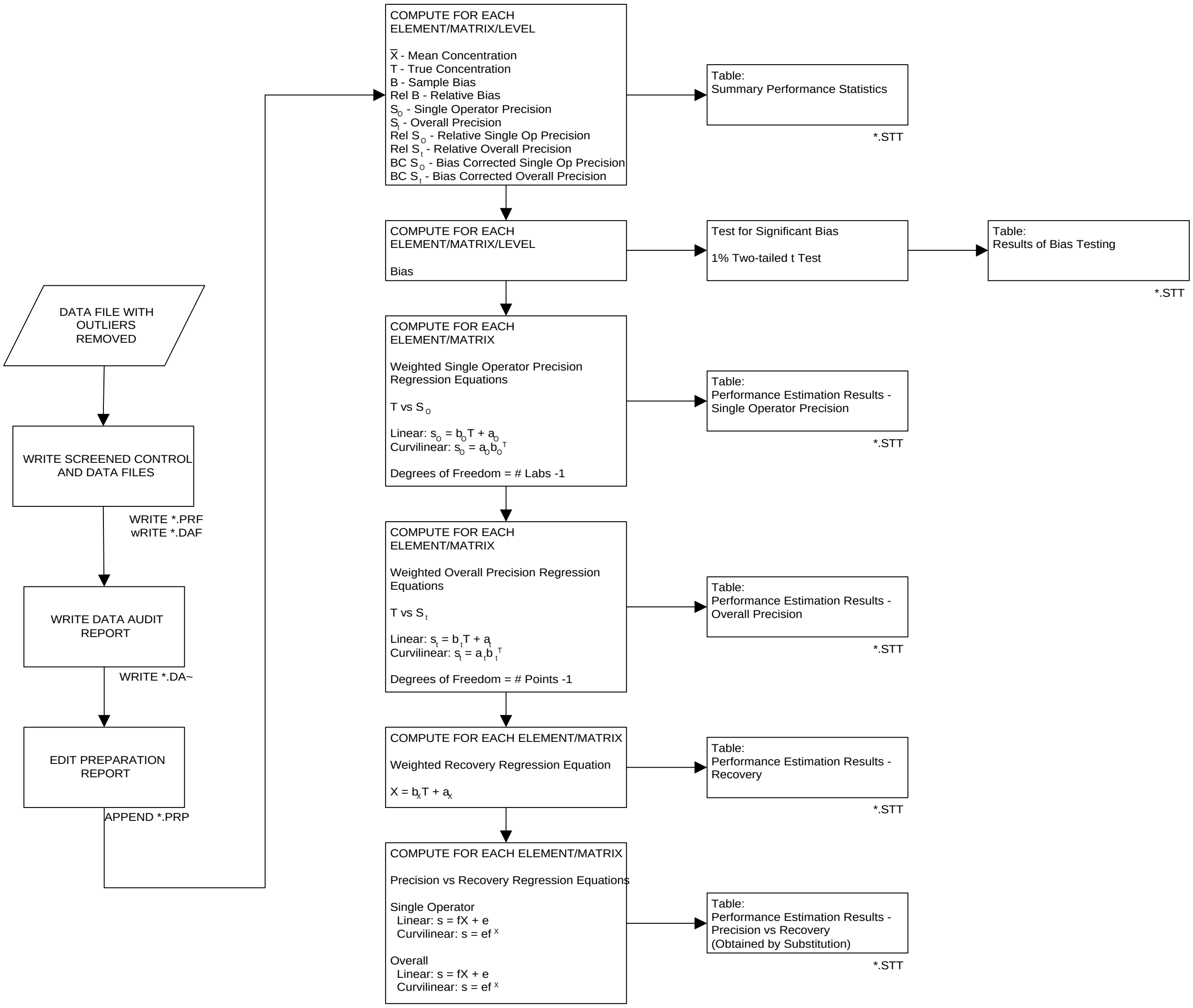


Figure 6-3 STATCALC Statistical Processing

Program Capacities:

Number of Elements	1
Number of Laboratories	100
Number of Youden Pairs	5
Number of Replicate Concentration Levels	9
Number of Replicates per Level	7
Number of Matrixes per Run	1
Number of Data Sets	1

6.1.1 *Notation for STATCALC*

Users may freely specify, under the limitations of the Personal Computer operating system, a file name "root" of up to eight characters which precedes the "." which separates the file name root from its three letter "extension." STATCALC uses this user specified root, referred to as "*" in the following discussions, to systematically name all of the intermediate and final input and output files created during processing with this same root name. The following files, with the exception of the data (*.DAT) and parameter (*.PRM) files which the user must create for each analyte/matrix, are created during STATCALC data processing. They are discussed in more detail in the following sections.

*.PRM	Of the two files that STATCALC must have, the first is a control file called the parameter (*.PRM) file. This file contains information about the type of analyte under study, the analytical method being used, the name of the matrix, the spike levels, units of measurement, and so forth.
*.DAT	The second file is the data (*.DAT) file which contains the laboratories' reported results and associated identification indexes for the analyte/matrix described in the parameter file.

*.DA~	Data that are read initially from the *.DAT file are echoed to an intermediate file (*.DA~), which provides an audit record of the actual data the program analyzes.
*.PRF	This file is a copy of the parameter file used for actual final processing, and amounts to a reconciliation of the *.PRM and *.DAT files.
*.DAF	After all checking has been accomplished, a file containing only non-rejected data is created (*.DAF). This file represents the final data set. It is used in the performance evaluation section of the program where precision and bias are estimated and reported.
*.PRP	The data preparation file, *.PRP, tracks the data preparation steps. After reading the *.PRM and *.DAT files, STATCALC first screens the data and reports possible transcription or calculation errors in the raw data file, *.DAT. Results of the lab ranking test as well as results of individual outlier testing are reported in the *.PRP file. The individual outlier test assumes that the underlying statistical population follows a normal probability model, and the results of normality testing are recorded in this file.
*.STT	The results of the summary statistic calculations are written in the statistical processing output file, *.STT, as are results of bias testing, estimation and performance regressions.
*.RGC	A file of regression coefficients is produced for use as input to other programs.
*.MEF *.MDT	Matrix effects testing (optional for pairs of matrices) produces two files, *.MEF for results of the test, and *.MDT for internal program use.

6.1.2 *Data Notation*

An observation (also called a result, recovery, measurement, observed value, data value, or data point) is the actual numerical value of the analyte concentration as reported by the laboratory. The letter "X" is used as generic notation for these reported values.

When appropriate, or necessary, the subscript "a" will be used to denote measurements for different analytes, the subscript "m" for different matrixes, the subscript "c" for different concentration levels, the subscript "l" for different laboratories, the subscript "r" for different replicates. In all cases, unless noted otherwise, the lower limits are 1 and the upper limits are the corresponding upper case letters of the respective categories of subscripts, that is:

Observation Hierarchy
Analyte: (a = 1,2,...,A)
Matrix: (m = 1,2,...,M)
Concentration Level: (c = 1.,2,...,C)
Laboratory: (l = 1,2,...,L)
Replicates: (r = 1,2,...,R)
Youden Pairs: r=1

The notation for a completely specified observation would be:

Observation (Recovery)
X_{amclr}

The letter "T" is used as generic notation for the true concentration of the analyte. Since there are "C" different concentration levels, the set of concentration levels (T) and incremental spikes (ΔT_c) would be denoted:

True Analyte Spikes and Concentrations
Error! Objects cannot be created from editing field codes., c=1,2,...,C
T_c, c=1,2,...,C

Subscripts used in the text following are suppressed when not needed, as in (X_{clr}). This is usually sufficient since with one analyte, a and A equal 1, and with a single matrix, m and M equal 1.

6.2 Data Validation

Data are screened and examined in various ways before being placed in a data bank and used for estimating population parameters or making decisions. To this end, data that are read initially from the DAT file are echoed to an intermediate file (*.DA~) and, optionally, to the screen. This operation provides an audit record of the actual data the program analyzed. It also serves to isolate the user provided data file (*.DAT) from program alteration and provide data to the next step in the analysis.

6.2.1 *"Zero" Data*

"Zero" data are not noted by the program as unusual and are treated in the same way as other nonzero measurements.

6.2.2 *Censored or "Less Than" Data*

Measurements which were reported as "less than" a particular value are handled by STATCALC as follows. A single character "flag field" is provided in the *.DAT (input data) file for each reported value. The program checks for a "<" symbol in the flag field and, optionally, ignores the flag (treats the value as if it were measured at the censoring level) or substitutes a 0.0, depending on the result of a query to the user. The program, as written, treats such values as being reported at the upper limit or lower limit (0.0) of the possible range.

6.2.3 *"Negative" Data*

"Negative" observations are values reported as negative by a laboratory. They are handled by the program as valid data values. That is to say, the program does not preclude processing negative reported values.

6.3 “Factor of 5” Data Screening

Mistranscriptions of data such as transposition errors, misplaced decimal points, or inadvertently misreported units will interfere with the statistical estimates of precision and bias produced by STATCALC. To guard against this, the data are initially screened for patently obvious inconsistencies. STATCALC does not remove any data during this screening procedure but flags it for the user's review.

6.3.1 *The Screening Procedure*

After reading the *.PRM (processing control file) and *.DAT files, the program screens each measurement of a given analyte in a given matrix for possible transcription or clerical errors by two methods. If a value is more than five times the mean result of values from all laboratories at that concentration level, or less than one-fifth that mean, it is reported as a questionable observation.

Since the above method will not work with data sets having negative values, the program also computes the Mean Absolute Deviation, *MAD*, for each level, i.e.,

$$MAD = \frac{\sum\left|X - \overline{X}\right|}{N} \qquad \text{(eq. 2)}$$

where $\overline{X}$ is the sample mean of all N results at a given level. It then calculates the individual deviation

$$\left|X - \overline{X}\right| \qquad \text{(eq. 3)}$$

for each value and checks if

$$\frac{\left|X - \overline{X}\right|}{MAD} \qquad \text{(eq. 4)}$$

is greater than 5.0.

The program reports all questionable observations and their associated identification information to the user in the data preparation result file, *.PRP. If no such observations are encountered, that fact is also recorded in the data preparation result file. No data are removed by the screening tests. The user must evaluate each questionable observation and correct any errors in the data in the *.DAT file. If any such corrections are necessary, the data processing must be initiated again using the corrected *.DAT file. After all individual values have been screened, processing of the data in the *.DAT file proceeds to the lab ranking routine.

6.4 Lab Ranking

After the data set is screened initially for transcription errors and the like, it is subjected to a statistical procedure designed to detect laboratories whose results as a whole are either so consistently high or so consistently low, compared to the other laboratories, as to be considered unreasonable. Results from such a laboratory should be rejected for a given analyte and matrix. If the laboratory's data are allowed to remain in the analysis, it will materially affect the precision and bias estimates, and the results of the analysis will not be representative.

6.4.1 *Rationale for the Test*

If a particular laboratory is producing exceedingly biased results that are consistently lower or higher than the other laboratories, and if the results from that laboratory are ranked among the other laboratories' results, the suspect laboratory will tend to get either consistently high or consistently low ranks. The measurements for a laboratory which has no such large systematic bias should rank randomly among the other laboratories' results, receiving some high ranks and some low ones. The statistical procedure which is used to test for outlying laboratories uses the sums of the several laboratories' ranks over several concentrations as the test statistic. If any given laboratory's sum is too large or too small, that laboratory may be excluded from the analysis.

STATCALC operates with a limit of no more than 20 percent of the laboratories removed by laboratory ranking. If the program detects that more than 20 percent of the laboratories need to be considered for rejection from the study, the operator is given a choice to keep the data from a laboratory that has failed the laboratory ranking test.

6.4.2 *Discussion of the Test*

The results of each laboratory at each concentration level are ranked in ascending order with the lowest value assigned “1” and the highest value the rank of “L”. If one or more observations are tied, each laboratory is given the average of the sum of the ranks of the equal observations. Rank sums are computed by summing across all concentrations for each laboratory. If the minimum rank sum is less than the lower critical value, or the maximum rank sum is larger than the upper critical value, then laboratories with those extreme sums are rejected. If no more than 20 percent of the laboratories are rejected, and if the operator does not retain data from a laboratory that failed the laboratory ranking test, their data are excluded. Their data are not used in any further analysis and are flagged with an "r" in the data validation file (*.DA~). The quantities needed for the lab ranking test and the test's results are reported in *.PRP in the laboratory ranking section of the file.

As a general rule, to perform the laboratory ranking procedure, the analyst must have a complete set of data. That is, every laboratory must have at least one observation at each concentration level for replicate data or both members of each pair for the Youden pair analytical design. In the case of missing data, an estimation procedure is used. If there are measurements reported for at least three different concentration levels (one member of each of three pairs for Youden paired data) for a given laboratory, the ranking subroutine fits a simple linear regression to the actual values reported for that laboratory. The estimation procedure returns estimated recoveries from its regression line to be used in place of the missing observations. Values substituted for missing observations are used only in the laboratory ranking routine are discarded before subsequent data processing.

If there are fewer than 15 laboratories involved, the critical values for the rank sums are those found in ASTM D 2777-86 (1). If there are more than 15 laboratories, the critical values for the laboratory rank sums are computed using an approximating uniform probability distribution to calculate the quantity Q below. The data for a laboratory are rejected and not used in subsequent calculations if the laboratory's rank sum satisfies either of the inequalities below:

$$Rank\,Sum < C + Q \tag{eq. 5}$$

or

$$Rank\,Sum < C \times L - Q \tag{eq. 6}$$

where

C = Number of Concentration Levels in the study

L = Number of Laboratories

and

$$Q = L\left(\frac{aC!}{2L}\right)^{1/C} - \left(\frac{C+1}{2}\right) \qquad \text{(eq. 7)}$$

where

α = Significance Level of the Test = 0.05 (Default)

6.4.3 *Justification for Use of the Test*

This laboratory ranking procedure is the standard in general use for evaluating data from interlaboratory studies presented in ASTM Standard D2777.

6.5 Testing for Outliers

The next step in the data analysis is to check those data remaining following rejection of laboratories for individual outlying observations, that is, individual recoveries for a given concentration that differ markedly from the other observations for that concentration, i.e., by an amount that cannot be explained solely by sampling variability. Such observations occur when a major disturbance (such as a radical deviation from standard procedure or an error in calculation or recording of the value) impacts the measuring process so as to grossly affect the accuracy of the measurement. These observations should be excluded from the subsequent analysis provided that either a) it is known that a substantial departure from prescribed experimental procedure has occurred, or b) a valid statistical criterion shows them to be outlying.

Because the program may exclude too many values from small data sets, a limit of 10 percent is imposed on the number of the values automatically excluded by this test. After 10 percent of the outliers have been removed, the operator is queried for the choice of retaining or discarding data that failed the outlier test.

6.5.1 *Rationale for the Test*

It is reasonable to expect variability from one measurement to another for a given concentration because of a certain amount of imprecision in the measurement process. However, when a major discrepancy between measurements occurs, the extreme value is no longer representative of the regular measurement process and should be eliminated from the collaborative analysis. The judgment as to whether a given observed recovery is so disturbed is based on determining how far that result lies from the average of all measured results for that concentration. A two-sided T test is used to determine whether the measurement lies too far from the average and should be rejected.

6.5.2 *Discussion of the Test*

As mentioned above, the statistical procedure which is used in STATCALC for individual outlier testing is based on comparing each individual recovery to the average of all laboratories' recoveries at a given concentration level in a given matrix.

Individual Outlier Detection Procedure

Step 1 - The distance of each individual recovery from the overall average is compared to the average distance of all recoveries as measured by the overall (also called "total", or "multiple laboratory operational") standard deviation, s_t.

For a given concentration level, with L laboratories and one replicate (for Youden pairs, the test is done for each pair level), the average recovery is computed as

$$\overline{X} = \frac{\sum_{l=1}^{L} X_l}{L} \qquad \text{(eq. 8)}$$

and the overall standard deviation as

$$s_t = \sqrt{\frac{SS_t}{L-1}} \qquad \text{(eq. 9)}$$

where

$$SS_t = \sum_{l=1}^{L} X_l^2 - \frac{\left(\sum_{l=1}^{L} X_l\right)^2}{l} \qquad \text{(eq. 10)}$$

Step 2 - To run the test, the distance of the most extreme observation from the overall average is computed, and divided by the overall standard deviation. The test statistic is

$$T = \max \frac{\left|X_l - \overline{X}\right|}{s_t} \qquad \text{(eq. 11)}$$

and the value associated with this maximum is discarded if T exceeds the critical value of *T* for a given level of significance alpha, (Default:5%) and number of observations equal to the current number of retained data for the given concentration level and matrix. Whenever such a rejection takes place, the pertinent information is recorded in *.PRP.

Step 3 - The test is conducted in the same manner for each and every concentration level, until all the data have been examined. The results of the outlier testing procedure are reported in *.PRP, in the outlier testing section of the file. After all checking has been accomplished, a file containing only nonrejected data is created (*.DAF). This file represents the final data set. It is used in the performance evaluation section of the program where precision and bias are estimated and reported. In all there are four files created by STATCALC's data preparation phase:

*.PRP	Results of Data Preparation
*.DA~	Data Echo File for Audit Trail
*.DAF	Final Data for Analysis
*.PRF	Parameter File for Final Processing

6.5.3 *Justification for the Procedure*

The outlier detection method described above and employed in STATCALC is the standard in general use for such purposes. It is presented in ASTM Standard D2777-96, Section 10.4, (2) The procedure also appears in Grubbs (3), along with a general and informative discussion of the subject of statistical determination of outliers.

6.6 Testing for Normality

The test for individual outliers assumes that the underlying statistical population, that is, the population from which the observed measurements are drawn, follows a normal probability model. Much of the regression analysis performed later in the program also assumes normality (at least approximate) as well. The YOUDENPR subprogram checks this assumption for each set of data consisting of all nonrejected measurements of all labs within each analyte, matrix, concentration level. To check the assumption, one of two test procedures is used, depending on the sample size. If there are 50 or fewer observations remaining within an analyte, matrix, concentration level, the data are checked using the Shapiro-Wilk (W) test (4, 5). When more than 50 observations remain, D'Agostino's (D) test (6, 7) is used.

In both cases, the statistical procedure tests the null hypothesis that all data in the sample come from the same normally distributed population versus the alternative hypothesis that the population's probability distribution is not normal. While a decision not to reject the null hypothesis lends credence to the assumption that the underlying distribution is normal, it cannot be viewed as proof.

6.6.1 *The Shapiro-Wilk (W) Test (Sample Size <= 50)*

The theory used in the development of the Shapiro-Wilk test is complex, and the test statistic does not lend itself easily to intuitive interpretation. A complete technical discussion of the theory and development of the test is given in Shapiro and Wilk (4).

Discussion of the Test. The computation of the test statistic for the W test is accomplished in several stages.

Shapiro-Wilk Test Procedure -

Step 1 - First the number of observations to be tested is determined. There must be at least 3 observations in the data set in order for the test to be run.

Step 2 - Next, when N is 50 or less, the data for the analyte-matrix-concentration under analysis is sorted into ascending order using a Shell-Metzner sort routine. The "sum of squares" (sum of squared deviations from the mean) of the data set being tested is then computed from the formulas below. Let R_l, l=1,2,...,L be the number of retained values for the L laboratories, for the selected analyte-matrix-concentration level. Then renumber the observations

$$X_{(i)}, i = 1,2,\ldots,N \qquad \text{(eq. 12)}$$

where the use of parentheses (1), (2), ... indicates that the array has been sorted into ascending order (so that $X_{(1)}$ is the smallest observation, $X_{(2)}$ the second smallest, ...), and

$$N = \sum_{l=1}^{L} R_l \qquad \text{(eq. 13)}$$

The sum of squares, SS_{XX}, is, then,

$$SS_{XX} = \sum_{i=1}^{N} \left(X_{(i)} - \overline{X} \right)^2 = \sum_{i=1}^{N} X_{(i)}^{\;2} - \frac{\left(\sum_{i=1}^{N} X_{(i)} \right)^2}{N} \qquad \text{(eq. 14)}$$

Step 3 - Next the appropriate set of k coefficients,

$a_1, a_2, \ldots, a_k$

are taken from Shapiro and Wilk (4), where

$$k = \begin{cases} \dfrac{N}{2} \\ \dfrac{N-1}{2} \end{cases} \qquad \text{(eq. 15)}$$

Step 4 - Then the test statistic, W, is computed from the above quantities,

SS_{XX} $a_1, a_2, \ldots, a_k$, and the ordered X values, $X_{(1)}, X_{(2)}, \ldots, X_{(N)}$

from the formula

$$W = \frac{1}{SS_{XX}} \left[\sum_{i=1}^{k} a_1 \left(X_{(N-i+1)} - X_{(i)} \right) \right]^2 \qquad \text{(eq. 16)}$$

Step 5 - The test is run at the 5% significance level. It rejects the normality assumption if the value of W is too small, that is, less than the critical value for N data points.

Step 6 - The results of the normality test ("A" = Accept normality, the data pass the test; "R" = Reject normality, the data do not pass the test.) are reported to the normality testing section of the *.PRP output file.

Justification for the Procedure. The Shapiro-Wilk procedure is a standard method of testing for departures from normality. It is one of the most powerful methods available for such purposes. The original development work for the test was done by S. S. Shapiro and M B. Wilk, (4).

6.6.2 *D'Agostino's (D) Test (Sample Size > 50)*

For larger samples, when there are more than 50 data points involved, tables for the critical values of the Shapiro-Wilk statistic are not generally available. In that case, a test developed by R. B. D'Agostino (6, 7) is used. The program is currently restricted to no more than 500 data points for a single element-matrix-concentration level.

Discussion of the Test. The preliminaries in the calculation of D, the test statistic for D'Agostino's test, are similar to those for Shapiro-Wilk.

D'Agostino's Test Procedure -

Step 1 - The data are sorted into ascending order as with the Shapiro-Wilk test.

Step 2 - Next the maximum likelihood estimate of the standard deviation, s , of the data set is computed from the formulas below. (Note: The "maximum likelihood estimate of the standard deviation" is similar to the "sample standard deviation", the difference being that where the latter divides by (N-1) the former divides by N.) Let R_l, l =1,2,..., L be the number of retained results for the L laboratories, for the selected analyte-matrix-concentration level. Then renumber the observations, as with the Shapiro-Wilk test,

$$X_{(i)}, I = 1,2,\ldots, N \qquad \text{(eq. 17)}$$

where the use of parentheses (1), (2), ... indicates that the array has been sorted into ascending order (so that $X_{(1)}$ is the smallest observation, $X_{(2)}$ the second smallest, ...), and

$$N = \sum_{l=1}^{L} R_l \qquad \text{(eq. 18)}$$

As before, the sum of squares, SS_{XX} , is,

$$SS_{XX} = \sum_{i=1}^{N} \left(X_{(i)} - \overline{X} \right)^2 \qquad \text{(eq. 19)}$$

$$SS_{XX} = \sum X_{(i)}{}^2 - \frac{\left(\sum X_i \right)^2}{N} \qquad \text{(eq. 20)}$$

Where $\overline{X}$ is the sample mean

$$\overline{X} = \frac{\sum_{i=1}^{N} X_{(i)}}{X} \qquad \text{(eq. 21)}$$

The maximum likelihood estimate of the standard deviation is then,

$$s' = \sqrt{\frac{SS_{XX}}{N}} \qquad \text{(eq. 22)}$$

Step 3 - Next, D, the preliminary form of the test statistic is computed:

$$D = \frac{N\sum_{i=1}\left[i - \frac{(N-1)}{2}\right]X_{(i)}}{N^2 s'} \qquad \text{(eq. 23)}$$

Step 4 - Then the actual test statistic, Y, is computed from the formula

$$Y = \frac{D - 0.28909479}{0.02998598 \big/ \sqrt{N}} \qquad \text{(eq. 24)}$$

Step 5 - The test is run at the 5% significance level, it rejects the normality assumption if the value of Y is too small, i.e., less than the 2.5 percentage point, or if Y is too large, greater than the 97.5 percentage point.

Step 6 - The results of the normality test ("A" = accept normality, the data pass the normality test", "R" = Reject normality, the data do not pass the normality test.) are reported to the normality testing section of *.PRP.

Justification for the Procedure. D'Agostino's development of the test for normality can be found in D'Agostino, (7).

6.7 Calculation of Analytical Method Performance Statistics

In the next step of the analysis, STATCALC calculates the sample summary statistics for precision, recovery, and bias as specified by D2777.

In addition, because they will be used in subsequent analyses, the program calculates bias-corrected, i.e., statistically unbiased, estimates of single operator and overall precision and includes these estimates in the output.

At this point in the analysis, the final data set consists of observations:

$$X_{cl}, = 1,2,\ldots C; l = 1,2,\ldots, L \qquad \text{(eq. 25)}$$

where

X_{cl} = measurement for the l th laboratory, at the c th concentration level

L = the number of retained laboratories after lab ranking

C = the number of concentration levels

R_{cl} = the number of retained measurements for laboratory l, at level c

These values are used in the calculations.

6.7.1 *Calculation of Method Mean Recovery and Bias*

Statistics are calculated for average recovery and bias.

Recovery. The mean recovery, $\overline{X}_c$, which is calculated for each concentration level, is found by averaging over the L sets of laboratory measurements at that level, i.e.,

$$\overline{X}_c = \frac{\sum_{l=1}^{L} X_{cl}}{N_{tc}} \qquad \text{(eq. 26)}$$

where

$$N_{tc} = \sum_{l=1}^{L} R_{cl} \qquad \text{(eq. 27)}$$

N_{tc} is the total number of retained observations among the L laboratories at concentration level c. With Youden pairs, R_{cl} is either 0 or 1. The notation "tc" is used here to be consistent with later notation requirements.

True Concentration. To calculate the true concentrations, the program accumulates the incremental spikes, ΔT_c, c = 1,2,...,C, given in the *.PRF file.

The value of the true concentration, T_c, for level c is given by

$$T_c = \sum_{i=1}^{C} \Delta T_i \qquad \text{(eq. 28)}$$

Bias. The sample bias, B_c, for concentration level c is defined as the difference between the true concentration and the mean recovery (D2777), i.e.,

$$B_c = \left(\overline{X}_c - T_c\right) \qquad \text{(eq. 29)}$$

The relative bias is then given by

$$(Relative\ Bias)_c = \frac{(\overline{X}_c - T_c)}{T_c} \times 100\% \qquad \text{(eq. 30)}$$

$$(Relative\ Bias)_c = \frac{B_c}{T_c} \times 100\% \qquad \text{(eq. 31)}$$

6.7.2 *Calculation of Method Precision Statistics (Standard Deviations)*

STATCALC computes estimates of the parameters of regression relating operator precision (s_o), overall precision (s_t), and method recovery (result), (X) to true concentration, (T). These regressions are:

Single Operator Precision regressions:

$$s_o = b_o T + a_o \qquad \text{(eq. 32)}$$

Overall Precision regressions:

$$s_t = b_t T + a_t \qquad \text{(eq. 33)}$$

Recovery regressions:

$$X = b_X T + a_X \qquad \text{(eq. 34)}$$

Single Operator Precision with Youden Pairs. The objective of the Youden pair design is to produce within laboratory measurements which are free from the analyst's tendency to make known replicates match. By selecting two concentrations that are nearly, but not exactly the same, and observing the difference between the uncorrelated measurements at the two concentration levels, the variance of this difference should be twice the variance of the individual measurements, i.e. twice the single operator precision which the analyst is attempting to estimate. If one assumes that single operator precision is equal for all laboratories, then the information (differences) for the several laboratories may be pooled to give a single operator precision estimate for each pair of observations.

Observations for the l^{th} laboratory (in a given data set, i.e., a given matrix/analyte combination) for the P pairs are

$$X_{lp1}, X_{lp2}; \quad p = 1, \ldots, P \qquad \text{(eq. 35)}$$

and the differences between the observations within pairs are

$$D_{lp} = \left(X_{lp1} - X_{lp2}\right); \quad p = 1, \ldots, P \qquad \text{(eq. 36)}$$

The estimate of the variance of D_{lp} is

$$\hat{s}_p^2 = \frac{\sum_{l=1}^{L_p} \left(D_{lp} - \overline{D}_p\right)}{\left(L_p - 1\right)} \qquad \text{(eq. 37)}$$

where

$$\overline{D}_p = \frac{\left(\sum_{l=1}^{L_p} D_{lp}\right)}{L_p} \qquad \text{(eq. 38)}$$

and L_p is the number of retained laboratories with both observations present (i.e. no outliers or missing values) for concentrations of pair p. D_{lp} is the difference between two observations, its variance is twice the single operator variance (assuming that the two observations in the pair are independent) so that the estimate of the single operator standard deviation for the pth pair is

$$s_{op} = \sqrt{\frac{\sum_{l=1}^{L_p} \left(D_{lp} - \overline{D}_p\right)^2}{2\left(L_p - 1\right)}} \qquad \text{(eq. 39)}$$

<u>Overall (Total) Precision for Youden Pairs</u>. Overall precision (S_{tc}) represents the total combined variability, i.e., both within and between laboratories. Let N_{tc} be the total number of retained observations among the L laboratories at concentration level c. Then

$$s_{tc} = \sqrt{\frac{\sum_{l=1}^{N_{tc}} \left(X_{cl} - \overline{X}_c\right)^2}{N_{tc} - 1}} \qquad \text{(eq. 40)}$$

Weights for the Precision Regressions. The STATCALC program uses explicitly weighted linear regression techniques which incorporate weights based upon 1) the number of retained data at a given concentration level and 2) the change in precision with concentration. The selected weights compensate for changing precision and rejected data to give approximately constant variances for the dependent variable at each concentration. The weights also compensate for "statistical bias" in the sample standard deviation, s, as an estimate of the true standard deviation.

Bias Factor (bf). Although a sample variance, $s^2_,$ is statistically unbiased for a true "population" single operator variance, s^2, its square root, s, is well known to be biased for s and can be corrected for bias with a multiplicative constant dependent upon sample size. To correct for this bias, each s is multiplied by a bias factor to give corrected estimates, $s^*_,$ of true precision,

$$s^* = (bf) \cdot s \qquad \text{(eq. 41)}$$

where

$$bf = \frac{1}{c_4} \qquad \text{(eq. 42)}$$

and

$$C_4 = \frac{\sqrt{\frac{2}{n}}\left(\frac{n-1}{2}\right)!}{\left(\frac{n-1}{2}\right)!} \qquad \text{(eq. 43)}$$

where n is the number of degrees of freedom with which the sample standard deviation is computed.

Standard Error Factor (sef). In addition, the standard error of the sample standard deviation, s, at a given concentration level, T, is also a function of the constant $c_{4.}$

$$s_{s|T} = \sqrt{1 - c_4^2} \cdot s_{X|T} \qquad \text{(eq. 44)}$$

so that the standard error of s^* is

$$s_{s^*|T} = s_{(bf)\cdot s|T} \qquad \text{(eq. 45)}$$

$$= (bf) \cdot \sqrt{1 - c_4^2} \cdot s_{X|T} \qquad \text{(eq. 46)}$$

$$= (bf) \cdot (sef) \cdot s_{X|T} \qquad \text{(eq. 47)}$$

which is a function of sample size and the true value of $s_{x|T.}$

Need for Weights. Since regression analysis requires homogeneity of variances for the dependent variable, weighted least squares estimates must be used to fit the regression model to the values of *s*. The weights used must be proportional to the variances of the *s* values for the different concentration levels. The appropriate weights are

$$w = \frac{1}{(bf)^2 \cdot (sef)^2 \cdot s_{X|T}^2} \qquad \text{(eq. 48)}$$

The true value of $s_{X|T}^2$ is not known, however, so it must be estimated.

Preliminary Weights. There is a practical difficulty here since the values of b and a are not determined until the regression line has been fit, yet their values are needed to determine weights used to fit the regression line. To overcome this difficulty, an initial rough estimate of the precision regression line is obtained by assuming that the true values of $s_{X|T}^2$ are constant, for which appropriate weights would be

$$w = \frac{1}{(bf)^2 \cdot (sef)^2} \qquad \text{(eq. 49)}$$

and weighted linear regression with these weights gives initial estimates, b_{init} and $a_{init,}$ of the slope and intercept, respectively, of the regression of s* on T.

$$s^* = b_{init} T + a_{init} \qquad \text{(eq. 50)}$$

Preliminary estimates of the method variance at each concentration level are now calculated using the values of b_{init} and $a_{init,}$ above. This calculation gives approximate weights

$$w = \frac{1}{(bf)^2 \cdot (sef)^2 \cdot (b_{init} T + a_{init})^2} \qquad \text{(eq. 51)}$$

which are then normalized, i.e. they are divided by their sum to give normalized weights, w_c

$$w_c \rightarrow \frac{w_c}{\sum_{c=1}^{C} w_c} \quad \text{(eq. 52)}$$

As before, the bias and standard error factors are determined for the number of degrees of freedom with which the standard deviation is computed.

Refined estimates of the precision regression equation are now obtained using the preliminary weights above to perform a second weighted linear regression for the precision model using the weighted regression formulas in the next section with Y = s*, X = T to give

$$\hat{s}^* = bT + a \quad \text{(eq. 53)}$$

<u>Weighted Linear Regression Formulas</u>. The formulas for computing weighted least squares regression estimates are similar to those for unweighted least squares. Suppose one has *C* observations on variables *U* (dependent) and *V* (independent), i.e.,

$$(V_c, U_c); \quad c = 1,2,\ldots,C \quad \text{(eq. 54)}$$

Then the weighted least squares estimates, given normalized weights

$$w_c; \quad c = 1,2,\ldots,C \quad \left(\sum w_c = 1.0\right) \quad \text{(eq. 55)}$$

and letting

$$WSS_{VU} = \sum w(V - \bar{V})(U - \bar{U}) = \sum wUV - \left(\sum wV\right)\left(\sum wU\right) \quad \text{(eq. 56)}$$

$$WSS_{VV} = \sum w(V - \bar{V})^2 = \sum wV^2 - \left(\sum wV\right)^2 \quad \text{(eq. 57)}$$

are

$$b = \frac{WSS_{VU}}{WSS_{VV}} \quad \text{(eq. 58)}$$

and

$$a = \overline{U} - b\overline{V} \tag{eq. 59}$$

where

$$\overline{V} = \sum wV \tag{eq. 60}$$

and

$$\overline{U} = \sum wU \tag{eq. 61}$$

and all sums are taken from 1 to C.

Precision Estimates by Weighted Curvilinear Regression. The STATCALC program uses essentially the same techniques described for the linear models described above to fit a curvilinear regression mode. To accomplish the curvilinear fit, the logarithms of the precisions are used, rather than the precisions themselves. The logarithmic form of the curvilinear precision equation is

$$\ln \hat{s}^{*} = bT + a \tag{eq. 62}$$

After the fitting is done, the logarithmic model is converted back so that it is expressed in the original (nonlogarithmic) units. Use of the curvilinear model assumes that operator precision changes at a constant relative rate.

The nonlogarithmic form of the model is

$$\hat{s}^{*} = a'(b')^{T} \tag{eq. 63}$$

where

$$b' = e^{b} \tag{eq. 64}$$

and

$$a' = e^{a} \tag{eq. 65}$$

General. For the curvilinear single operator regressions, the dependent variable is the logarithm of the bias corrected precision, i.e.,

$$\ln \hat{s}^{*}_{oc}; \quad c = 1,2,\ldots,C \qquad \text{(eq. 66)}$$

and the true concentration is the independent variables, i.e.,

$$T_c; \quad c = 1,2,\ldots,C \qquad \text{(eq. 67)}$$

Weighted linear regression is used, but, since the standard deviation of s* is proportional to the standard deviation of $\sigma_{X|T}$, the logarithmic transformation stabilizes the variance. The regression weights depend only on the number of retained data. In general, they are

$$w = \frac{1}{(bf)^2 \cdot (sef)^2} \qquad \text{(eq. 68)}$$

Recovery Estimates by Weighted Linear Regression. Recoveries are the measured amounts, X, reported by the laboratories. In fitting the regression models, it is assumed that, at a given concentration, the expected recovery is the same for all laboratories. STATCALC estimates the parameters of a linear model which relates recovery to true concentration.

$$\hat{X} = bT + a \qquad \text{(eq. 69)}$$

For estimating the recovery regression equation, STATCALC uses weighted regression techniques for the same reasons already discussed for precision regression, that is, to compensate for decreasing precision and rejected data to give approximately constant standard errors for recovery at each concentration.

The recovery regressions are performed with recovery as the dependent variable and true concentration as the independent variable. The actual calculations are performed on the C mean recovery-true concentration pairs, i.e.,

$$\left(T_c, \overline{X}_c\right); \quad c = 1,2,\ldots,C \qquad \text{(eq. 70)}$$

Weighted linear regression is used with (normalized) weights

$$w_c; \quad c = 1,2,\ldots,C \qquad \text{(eq. 71)}$$

Calculation of these weights differ from those for precision. To achieve the required homogeneity of variances the weights used must be proportional to the variances of the X values for the different concentration levels. The appropriate weights are

$$w = \frac{1}{N_T \cdot s_{X|T}^{2}} \qquad \text{(eq. 72)}$$

where N_T is the total number of retained observations from which the mean recovery is computed and $\sigma^2_{X|T}$ is the true overall precision. The true value of $\sigma^2_{X|T}$ is not known, however, so it must be estimated using $\hat{s}_T^*$ from the previous precision regression analysis.

The weights are

$$w_c = \frac{N_c}{\hat{s}_c^*} \qquad \text{(eq. 73)}$$

where $\hat{s}_c^*$ is the appropriate regression equation evaluated at T_c.

Weighted least squares with $U = \overline{X},\ V = T$ is used to obtain the recovery regression equation.

Precision Versus Recovery. A regression relationship between precision and recovery may be obtained by substituting the recovery regression results into the precision regression formulas.

Linear Models. The formulas output by the program for linear precision and linear recovery versus true concentration are:

- Single Operator Precision

$$\hat{s}_o^* = b_o T + a_o \qquad \text{(eq. 74)}$$

- Overall Precision

$$\hat{s}_t^* = b_t T + a_t \qquad \text{(eq. 75)}$$

- Recovery

$$\hat{X} = b_X T + a_X \qquad \text{(eq. 76)}$$

Solving for T in the recovery equation gives

$$T = \frac{(\hat{X} - a_X)}{b_X} \tag{eq. 77}$$

which is substituted into the precision equations to obtain

$$\hat{s}^* = a_o + b_o \frac{(\hat{X} - a_X)}{b_X} \tag{eq. 78}$$

$$= \left(a_o - \frac{a_X}{b_X} \right) + \frac{b_o}{b_X} \hat{X} \tag{eq. 79}$$

$$= e_o + f_o \hat{X} \tag{eq. 80}$$

where

$$e_o = a_o - \frac{a_X}{b_X} \tag{eq. 81}$$

$$f_o = \frac{b_o}{b_X} \tag{eq. 82}$$

In a like manner, for the overall precision,

$$\hat{s}_t^* = e_t + f_t \hat{X} \tag{eq. 83}$$

where

$$e_t = a_t - \frac{a_X}{b_X} \tag{eq. 84}$$

$$f_t = \frac{b_t}{b_X} \tag{eq. 85}$$

Curvilinear Models. The formulas output by the program for curvilinear precision and linear recovery versus true concentration are:

- Single Operator Precision

$$\hat{s}_o^* = a_o(b_o)^T \qquad \text{(eq. 86)}$$

- Overall Precision

$$\hat{s}_t^* = a_t(b_t)^T \qquad \text{(eq. 87)}$$

- Recovery

$$\hat{X} = b_X T + a_X \qquad \text{(eq. 88)}$$

Solving for T in the recovery equation gives

$$T = \frac{(\hat{X} - a_X)}{b_X} \qquad \text{(eq. 89)}$$

which is substituted into the single operator precision equation to obtain

$$\hat{s}_o^* = a_o(b_o)^{(\hat{X} - a_X) / b_X} \qquad \text{(eq. 90)}$$

$$\hat{s}_o^* = a_o(b_o)^{\left(-\frac{a_X}{b_X}\right)}(b_o)^{\left(\frac{\hat{X}}{b_X}\right)} \qquad \text{(eq. 91)}$$

$$\hat{s}_o^* = e_o(f_o)^{\hat{X}} \qquad \text{(eq. 92)}$$

where

$$e_o = a_o(b_o)^{\left(-\frac{a_X}{b_X}\right)}(b_o)^{\left(\frac{\hat{X}}{b_X}\right)} \qquad \text{(eq. 93)}$$

$$f_o = (b_o)^{\left({}^{1}\!/\!{}_{b_X} \right)} \qquad \text{(eq. 94)}$$

In a like manner for the overall precision,

$$\hat{s}_t^* = e_t\left(f_t\right)^{\hat{X}} \qquad \text{(eq. 95)}$$

6.8 Testing for Significant Bias

The program next performs the necessary calculations and tests to determine whether the observed bias values for each level are statistically significant.

6.8.1 *General*

The statistical procedure tests the null hypothesis that the true method bias at each concentration is zero, versus the alternative that it is nonzero, assuming the underlying distribution is normal. While a decision not to reject the null hypothesis is not proof that the method bias is zero, it lends credence to such a conclusion.

6.8.2 *Rationale for the Procedure*

If there is no method bias for a given level of concentration, then one would expect that the true and measured amounts of analyte should be the same, on average. A Student's t test procedure is used to judge, as prescribed by ASTM D2777, whether the bias (difference between true and average measured concentrations) for the sample data at each concentration level is within the realm of acceptable variability, taking overall method precision into account. First, the program adjusts the overall precision (standard deviation) to reflect the number of observations over which recovery was averaged at the given concentration level. The adjusted value is called the standard deviation of the mean. Then, the program calculates the number of standard deviations (of the mean) by which the true and average recovered values differ. Finally, this latter figure is tested for acceptability under Student's t distribution.

6.8.3 *Outline of the Calculations*

The basic steps in the calculations at each concentration level are given below.

Student's t Test for Bias -

Step 1 - Calculate the bias:

$$B_c = \overline{X}_c - T_c \qquad \text{(eq. 96)}$$

Step 2 - Calculate the standard deviation of the mean (recovery):

$$s_{\overline{X}} = \frac{s_{tc}}{\sqrt{N_{tc}}} \qquad \text{(eq. 97)}$$

When the average of the Level 1 concentration recoveries is used as the true background concentration, an adjustment must be made in this calculation. The bias is then identically 0.0 for level 1 and for c greater than 1 it is

$$\overline{X}_c - T_c = \overline{X}_c - \overline{X}_1 - \sum_{i=2}^{c} \Delta T_i \qquad \text{(eq. 98)}$$

for which the standard deviation is estimated as

$$s_{\overline{X}_c - \overline{X}_1} = \sqrt{\frac{s_{tc}^2}{N_{tc}} + \frac{s_{t1}^2}{N_{t1}}} \qquad \text{(eq. 99)}$$

Step 3 - Calculate the observed t-value:

$$t_c = \frac{\left|\overline{X}_c - T_c\right|}{s_{tc} \big/ \sqrt{N_{tc}}} \qquad \text{(eq. 100)}$$

Step 4 - Determine the critical value, t $_{.005}$, for a 1% (two-tailed) significance level for Student's t test with N $_{tc}$ - 1 degrees of freedom, and compare t from Step 3 to the critical value. The null hypothesis is rejected (concluding there is significant bias) if

$$t_c > t_{.005} \qquad \text{(eq. 101)}$$

Step 5 - The results of the bias testing ("Yes" = "Yes, the bias is significant." or "No" = "No, the bias is not significant.") are reported to *.STT.

6.9 Use of STATCALC Output

The STATCALC output files, particularly the data preparation files (*.PRP) and statistical processing files (*.STT) provide all of the information necessary for the user to compile the tables and graphs required in ASTM D2777. Copies of the data, data preparation and statistical processing files for all of the AMQ-IV Round 2 data are contained in Appendix H. The precision and recovery regression equations are used to calculate the L_{CI} and AML discussed in Section 8. Section 9 contains the values calculated from the AMQ-IV Round 2 data.

6.10 References

1. American Society for Testing and Materials, "Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water", D2777-86, *Annual Book of ASTM Standards*, 1996.

2. American Society for Testing and Materials, "Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water", D2777-96, *Annual Book of ASTM Standards*, 1997.

3. F.E. Grubbs, "Procedures for Detecting Outlying Observations in Samples", Technometrics, 2, No. 1, February, 1969.

4. S.S. Shapiro and M. B. Wilk, "An Analysis of Variance Test for Normality", Biometrika, Vol 52, 1965, pp. 519-611.

5. S.S. Shapiro, M.B. Wilk and H.J. Chen, " A Comparative Study of Various Tests of Normality", Journal of the American Statistical Association, 63, 324, December 1968, pp. 1343-1372.

6. R.B. D'Agostino, "An Omnibus Test of Normality for Moderate and Large Samples", Biometrika, 58, 1971, pp. 341-348.

7. R.B. D'Agostino, "Small Sample Probability Points for the D Test of Normality", Biometrika, 59, 1972, pp. 219-221.

7

DATA EVALUATION

The AMQ-IV Round 2 validation effort was part of a comprehensive data collection and evaluation effort to provide a complete profile of the personnel, procedures, and methods used by utility laboratories for trace metal analysis. This section discusses the operation procedures employed by the participants and presents the results of the validation effort. The validation results are discussed by element and matrix.

7.1 Operating Data

During the AMQ-IV Round 2 test program, all the participants were sent a questionnaire concerning:

- Operator experience
- Analytical instrumentation
- Laboratory standards and sample handling
- Sample preparation and analysis

A copy of that form with highlights of the AMQ-IV Round 2 results from the eighteen participating laboratories summarized can be found in Appendix E.

From these documents, a profile of the personnel and procedures employed on the AMQ-IV Round 2 validation effort was constructed.

7.1.1 *Personnel Experience Levels*

Figure 7-1 shows the percentage of respondents having a given number of years of GFAAS experience. Thirty-eight percent had 1 to 5 years of GFAAS experience, twenty-eight percent had between 5 and 10 years of GFAAS experience and twenty-two percent had more than 10 years GFAAS experience. Only twelve percent of the operators had less than 1 year of GFAAS experience. Sixty percent of the analysts had attended GFAAS training classes for the specific instrument they used in AMQ-IV Round 2.

Figure 7-2 illustrates the education level of the analysts and supervisors. Seventy-two percent of the analysts had a BA/BS degree in chemistry, biology or a related field of study. One analyst had a MA/MS degree in chemistry. Eighty-nine percent of the supervisors had BA/BS degrees, 63% in chemistry with the remainder in biology,

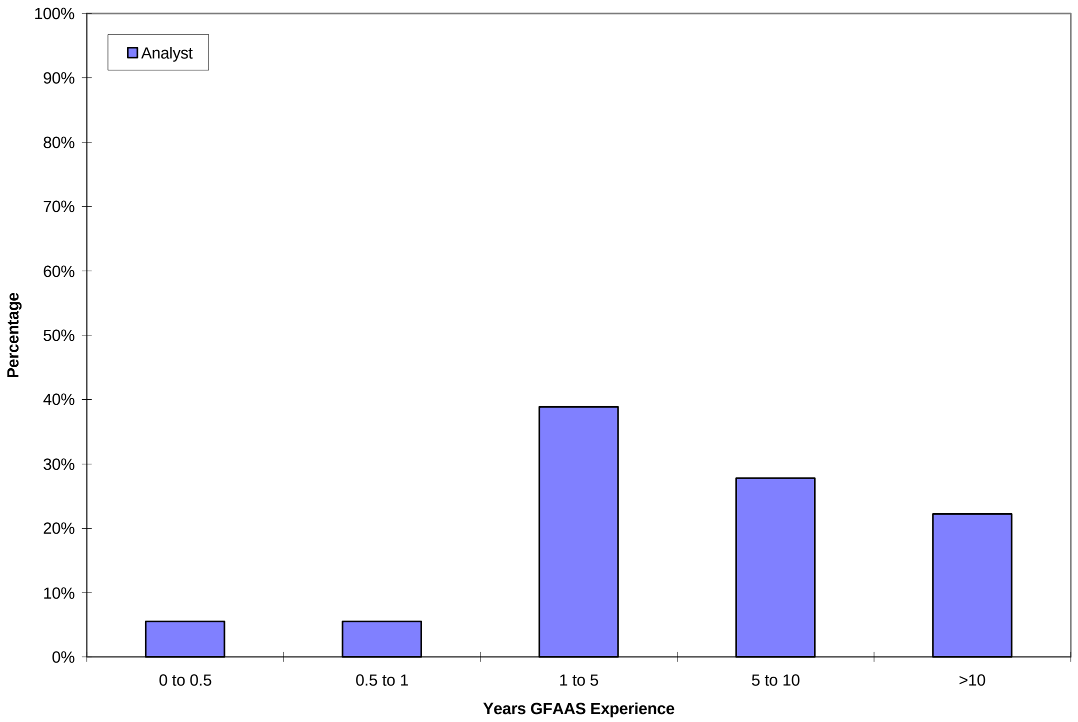


Figure 7-1 Operator GFAAS Experience

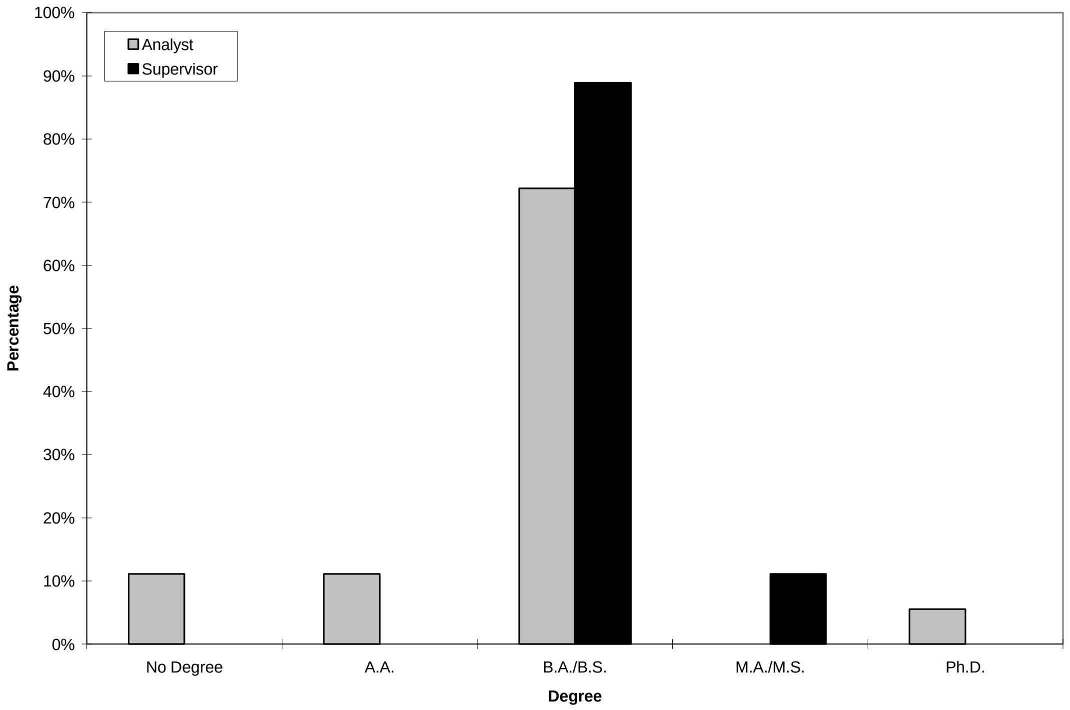


Figure 7-2 Comparison of Education: Analyst and Supervisor

biochemistry, microbiology, and environmental science. Eleven percent of the supervisors had MA/MS degrees in chemistry. Seventy-seven percent of the supervisors had more than 10 years experience. Only 11% had fewer than 5 years experience.

7.1.2 *Analytical Instrumentation*

Twenty-two instruments were used by the eighteen laboratories participating in AMQ-IV Round 2. Ninety percent employed autosamplers for sample introduction. The majority of the laboratories performed data reduction by comparison to a linear (52%) or non-linear (24%) calibration curve. One laboratory reported they used a least squares program for data analysis, two used a quadratic function, and one used "best fit".

Seventy-two percent of the laboratories analyzed all analytes using platform graphite furnace. Eleven percent of the laboratories used tube graphite furnace for all analytes. Seventeen percent used tube graphite furnace for some analytes and platform graphite furnace for others. Figure 7-3 illustrates the type of graphite furnace used by the participants.

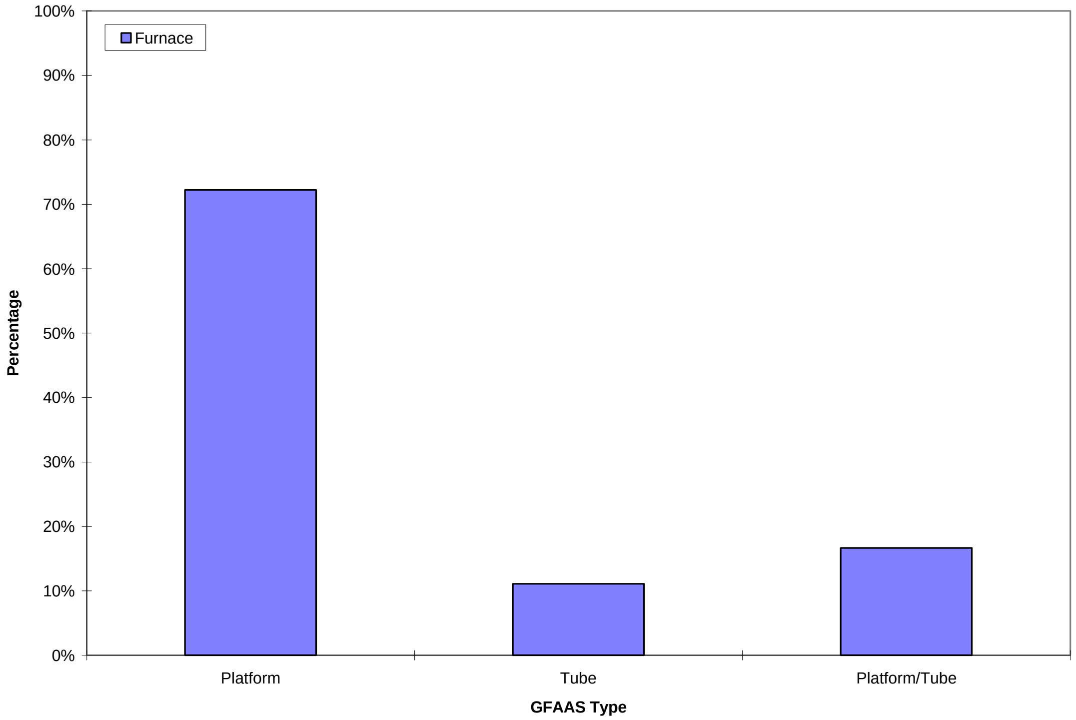


Figure 7-3 Comparison of Type of Graphite Furnace Used in AMQ-IV Round 2

7.1.3 *Laboratory Standards and Sample Handling*

All of the participants used commercially prepared standard reference materials for calibration.

7.1.4 *Sample Preparation and Analysis*

Only one laboratory noted the presence of precipitates in any of the sample aliquots after digestion and redilution. The laboratory observed precipitates in some of the estuarine and acid mine drainage samples. The samples were allowed to settle and the supernatant was used. Another laboratory noted that they vacuum filtered samples in the study, although they did not indicate that they had observed any precipitates.

One-third of the analysts added matrix modifiers other than those listed in the test procedure during sample analysis. These included magnesium nitrate, palladium/magnesium nitrate, and ammonium phosphate.

7.2 Raw Data Analysis

As noted in Section 6, the results from each laboratory were input to a dBase III® data base from the AMQ-IV Round 2 reporting forms. Once the data were proofed for typographical errors, the appropriate ASCII files were generated for use by the STATCALC statistical program.

The following sections discuss the make-up of the data before and after processing.

7.2.1 *Raw Data*

A complete printout of the raw data by element is contained in Appendix G. The data were sorted by element, laboratory, matrix, and concentration level.

7.2.2 *Outlier Removal Results*

The AMQ statistical program, STATCALC, performs the two outlier removal activities described in ASTM D2777 (1): lab ranking and individual outlier removal. These are described in detail in Section 6. When a lab is ranked out, all of its data are removed for a particular element and matrix. Up to 20% of the laboratories may be removed by lab ranking.

The individual outlier test is performed on the remaining data by element, matrix and concentration level. A maximum of 10% of the data points may be removed by element, matrix and concentration level. For small data sets with fewer than 10 laboratories surviving the lab ranking test, a maximum of one outlier data point per concentration level may be removed.

Table 7-1 summarizes the total number of data points (summed over all concentration levels) remaining after outlier removal activities. The largest percentage of outliers was removed by the laboratory ranking test. Only a small percentage was removed by the outlier procedure.

Table 7-1
Data Points Remaining after Outlier Removal
(Percentages based on Total Data Points Received)

			After Lab Ranking		After 1% t-Test	
Element	**Matrix**	**Points as Received**	**Points**	**%**	**Points**	**%**
As	RGW	136	112	82.4	110	80.9
As	GW	170	140	82.4	134	78.8
As	EST	150	120	80.0	115	76.7
As	AMD	160	150	93.8	143	89.4
Cd	RGW	170	140	82.4	133	78.2
Cd	GW	170	140	82.4	136	80.0
Cd	EST	140	120	85.7	118	84.3
Cd	AMD	160	130	81.3	129	80.6
Cr	RGW	170	160	94.1	153	90.0
Cr	GW	170	150	88.2	145	85.3
Cr	EST	140	120	85.7	118	84.3
Cr	AMD	170	140	82.4	137	80.6

RGW = Reagent Grade Water
GW = Groundwater
EST = Estuarine
AMD = Acid Mine Drainage

7.2.3 *Normality Testing*

The statistical program, STATCALC, tested each of the data sets for normality using either the Shapiro/Wilk (sample size <50) or D'Agostino's (sample size > 50) normality test. These tests are discussed in detail in Section 6. The test for individual outliers and much of the regression analysis assumes at least approximate normality. The results of the normality tests are either A (accept normality, the data passes the normality test) or R (reject normality, the data does not pass the normality test). Table 7-2 summarizes the results of the normality tests. A total of 96 of the 118 data sets tested normal (81%).

Table 7-2
Data Distribution after Outlier Removal

Element	Matrix	B1	B2	1	2	3	4	5	6	7	8
As	RGW	-	-	A	R	A	A	A	A	A	A
As	GW	A	A	A	A	R	A	A	A	A	A
As	EST	A	A	A	A	A	A	A	A	A	A
As	AMD	R	R	A	A	A	R	A	A	A	A
Cd	RGW	A	A	A	R	A	A	R	R	A	A
Cd	GW	A	R	A	R	A	R	A	A	R	A
Cd	EST	R	R	R	A	R	A	A	A	A	A
Cd	AMD	A	A	A	A	A	A	A	A	A	A
Cr	RGW	A	A	A	A	A	R	R	A	R	A
Cr	GW	R	A	R	A	A	A	A	A	A	A
Cr	EST	A	R	A	A	A	A	A	A	A	A
Cr	AMD	A	A	A	A	A	A	A	A	A	A

RGW = Reagent Grade Water
GW = Groundwater
EST = Estuarine
AMD = Acid Mine Drainage

7.3 Reduced AMQ-IV Round 2 Data

The results of the statistical analysis of the AMQ-IV Round 2 data are contained in Appendix H. For each element, sorted by matrix, the following tables are present:

- Data File (.DAT) - Displays original raw data submitted by each laboratory.
- Data Validation File (.DA~) - Audit record documenting the fate of each original data point. Includes information on values removed by lab ranking and outlier testing.
- Final Data File (.DAF) - Final data set submitted for statistical processing after removal of outliers.
- Data Preparation File (.PRP) - Displays the results of the factor of 5 screening, laboratory ranking, individual outlier removal, and normality testing.
- Summary Statistics (.STT) - Contains recovery, single operator standard deviation, and overall standard deviation results at each concentration; results of bias testing; linear and curvilinear equations for single operator and overall standard deviation; linear regression equations for recovery; and linear regression equations for both single operator and overall standard deviation versus recovery (obtained by substitution).

These data were summarized and plotted for each element. The following plots are presented and discussed by element in this section:

- Single operator standard deviation versus true concentration (true concentration equals the mean of the lowest concentration plus the added spikes)
- Overall standard deviation versus true concentration
- Single operator relative standard deviation versus mean concentration
- Overall relative standard deviation versus mean concentration
- Mean result versus true concentration for all matrices. The 100% recovery line is plotted along with ± 10% lines.
- Mean result versus true concentration for each matrix. The linear regression through the data is plotted to illustrate linearity of the recovery.

7.3.1 *Arsenic*

The reduced data for arsenic are found in Appendix H.

Arsenic Standard Deviation. Figure 7-4 and 7-5 show the single operator and overall standard deviation data for arsenic. A Rocke-Lorenzato curve fit (see Section 8.3) across the concentration range analyzed is plotted for all data sets except the overall data for groundwater, which was best fit with an exponential curve. The low TDS matrices,

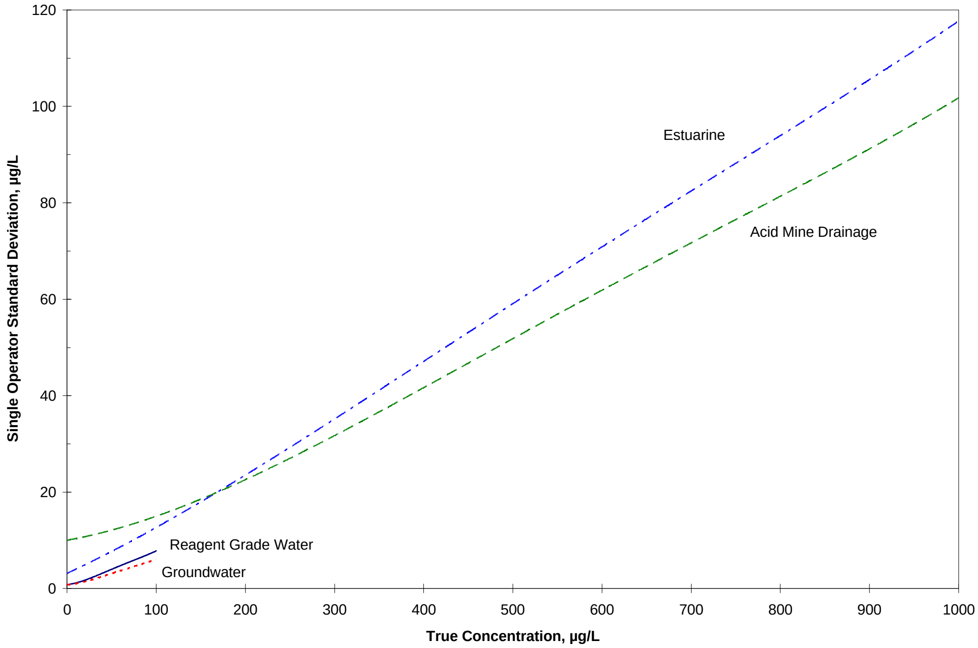


Figure 7-4 Plot of the single operator standard deviation versus the true concentration for arsenic by GFAAS

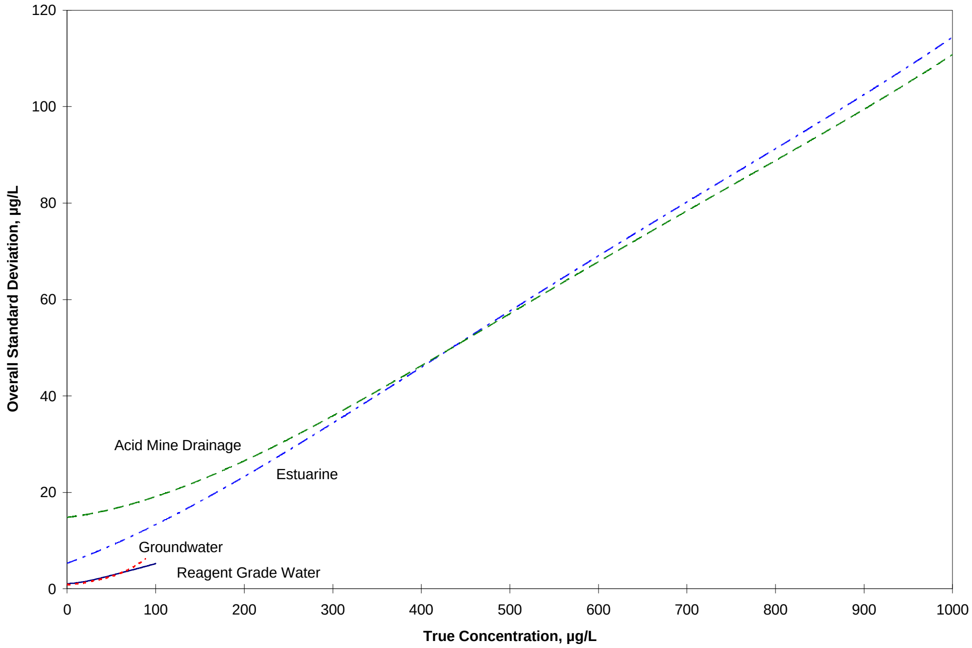


Figure 7-5 Plot of the overall standard deviation versus the true concentration for arsenic by GFAAS

reagent grade water and groundwater, exhibited similar trends in absolute standard deviation versus concentration. The high TDS matrices, estuarine and acid mine drainage, had higher standard deviations. The acid mine drainage matrix had the highest single operator standard deviation at low concentrations, but the estuarine matrix had the highest standard deviation above about 180 µg/L arsenic. The same pattern was observed in the overall standard deviation plot, with the crossover concentration at approximately 450 µg/L arsenic.

Figures 7-6 and 7-7 plot the single operator and overall relative standard deviation (RSD) against mean concentration for arsenic in all matrices. Note the log/log scale. As expected, the highest RSDs were obtained at the lowest concentrations. Single operator RSDs leveled off to generally less than 15% as concentration increased. Overall RSDs tended to be higher, particularly for the estuarine and acid mine drainage samples. For all matrices, overall RSDs were generally less than 20% at the higher concentrations.

Arsenic Recovery. The recovery data (mean result versus true concentration) for arsenic in all matrices are shown in Figure 7-8. The 100% recovery (solid line) and ±10% recoveries (dotted line) are shown for reference. By definition, recovery for the lowest concentration is 100% (reported mean = lowest true concentration). Recoveries for all matrices were within ±10%. Plots of the individual recoveries by matrix are found in Figures 7-9 through 7-12. The weighted linear regression through the data is shown. Arsenic recoveries were quite good for all matrices and concentrations.

7.3.2 *Cadmium*

The reduced data for cadmium are found in Appendix H.

Cadmium Standard Deviation. The single operator and overall standard deviation plots for cadmium are found in Figures 7-13 and 7-14. Reagent grade water exhibited the lowest absolute standard deviation across the concentration range studied. The standard deviation for groundwater was similar to that of reagent grade water at lower concentrations, but trended upward at higher concentrations. Single operator standard deviations for the estuarine and acid mine drainage samples were similar at the lowest concentrations, but estuarine standard deviations trended higher at higher concentrations. The overall standard deviation for the estuarine samples was lower than that of acid mine drainage at low concentrations, but was higher for estuarine samples above about 15 µg/L.

Single operator and overall RSDs for cadmium are shown in Figures 7-15 and 7-16. RSDs generally trended lower at higher concentrations. The overall RSDs exhibited a clustering of data at the higher concentrations with estuarine having the highest RSDs, followed by acid mine drainage, groundwater and then reagent grade water.

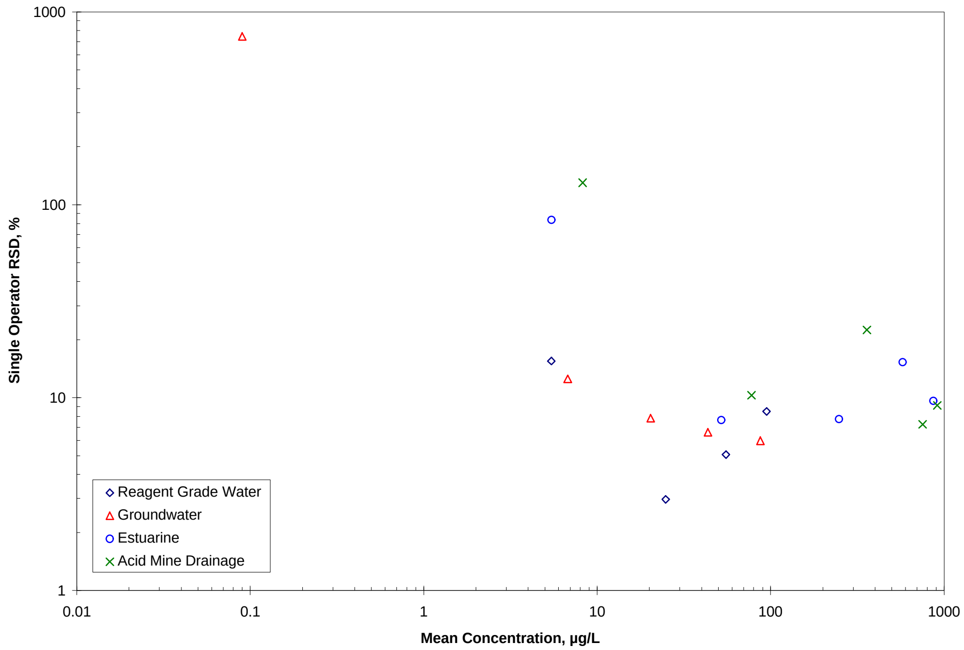


Figure 7-6 Plot of the single operator relative standard deviation versus the mean concentration for arsenic by GFAAS

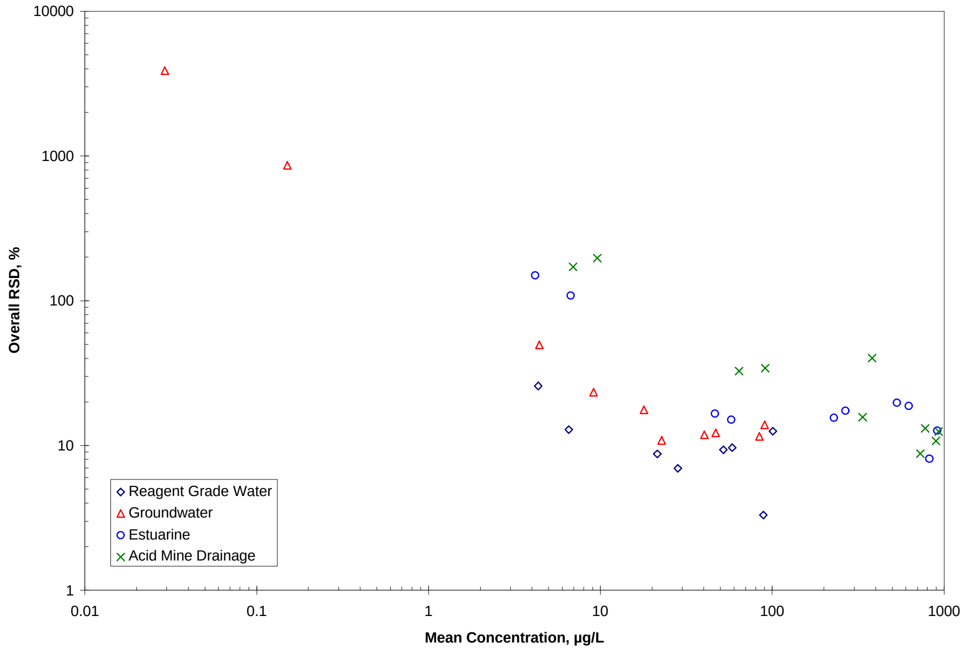


Figure 7-7 Plot of the overall relative standard deviation versus the mean concentration for arsenic by GFAAS

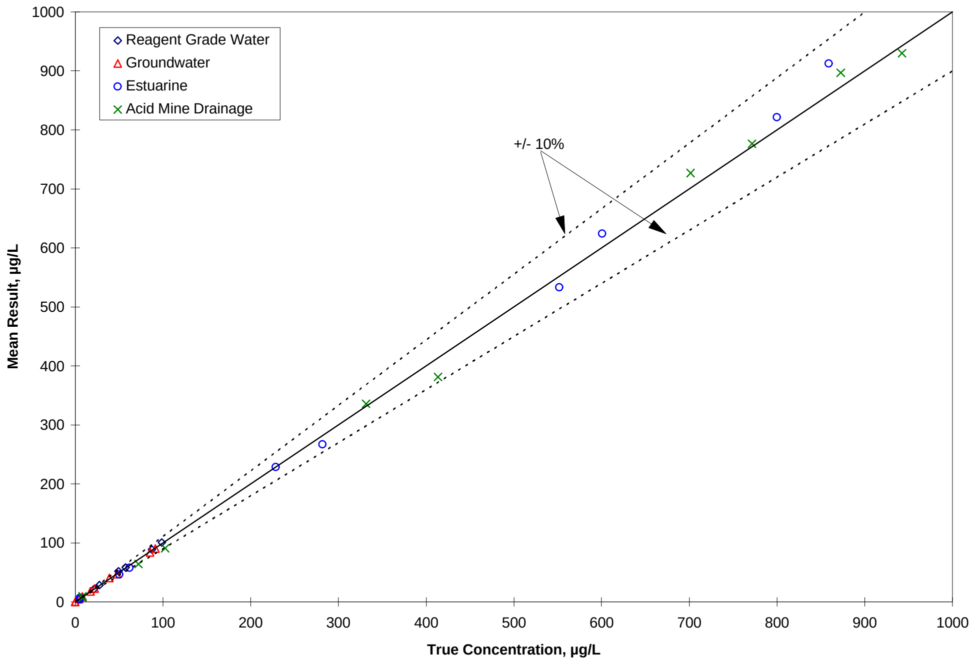


Figure 7-8 Plot of the mean result versus the true concentration for arsenic in all matrices by GFAAS

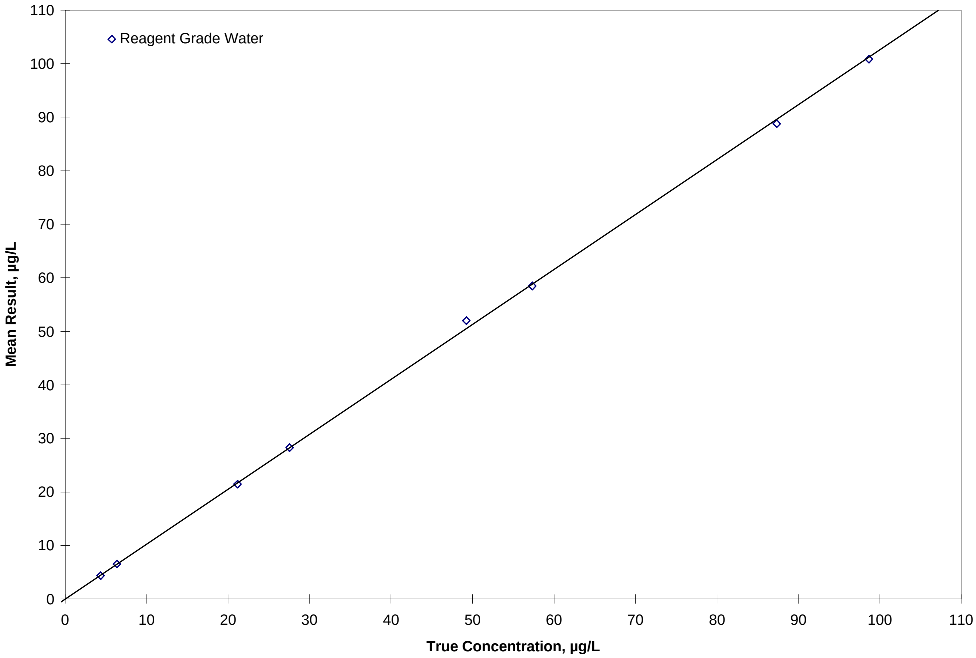


Figure 7-9 Plot of the mean result versus the true concentration for arsenic in reagent grade water by GFAAS

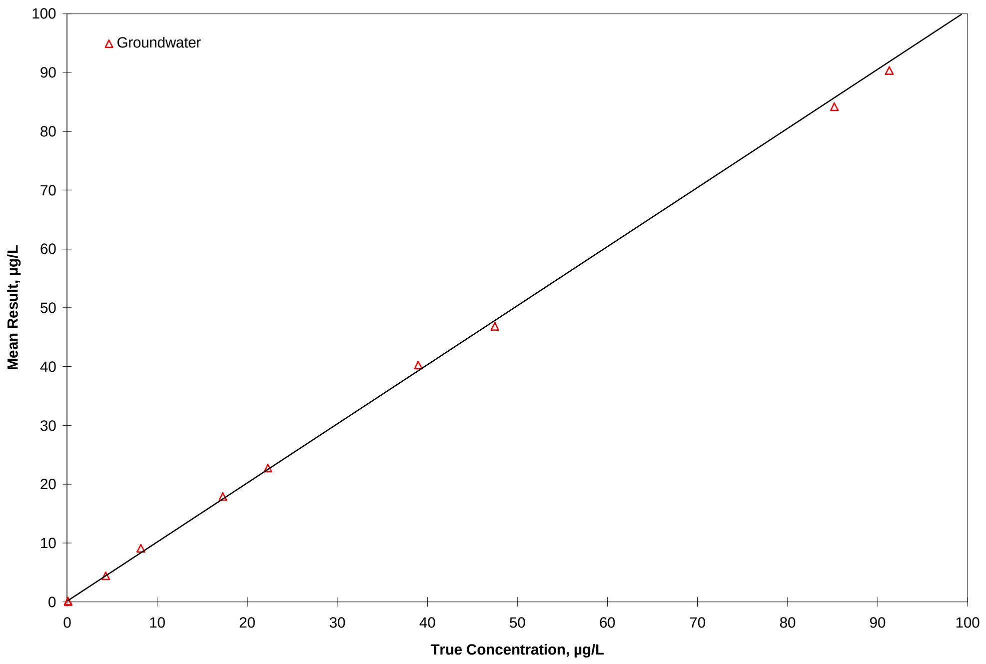


Figure 7-10 Plot of the mean result versus the true concentration for arsenic in groundwater by GFAAS

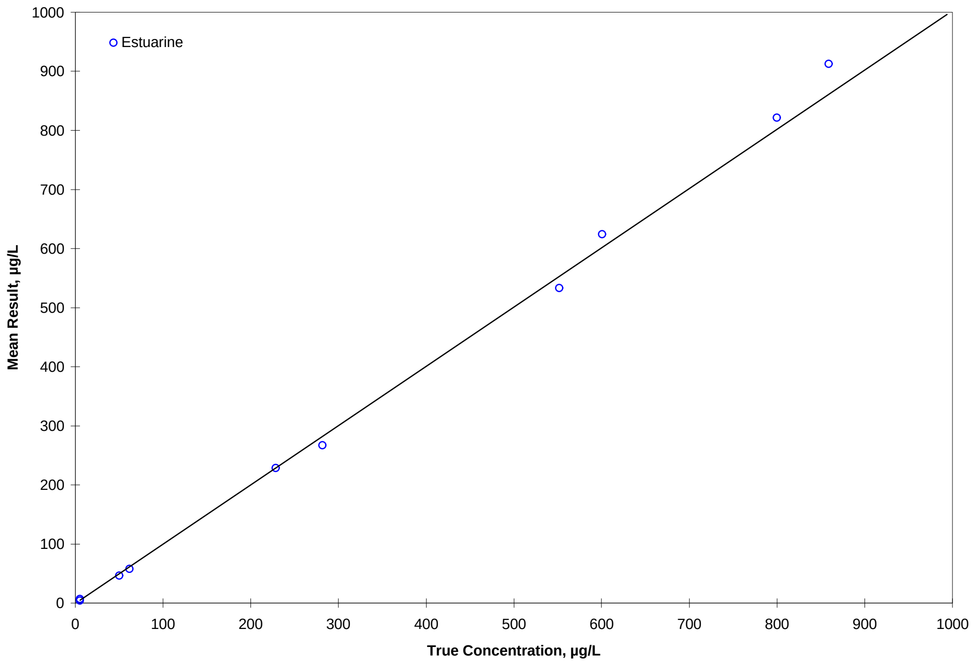


Figure 7-11 Plot of the mean result versus the true concentration for arsenic in estuarine water by GFAAS

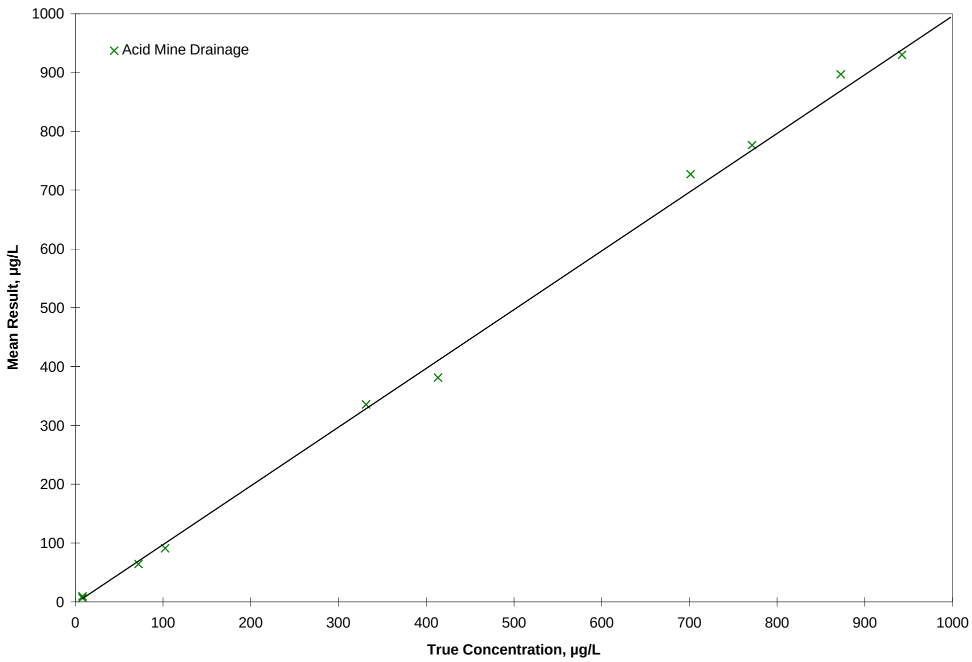


Figure 7-12 Plot of the mean result versus the true concentration for arsenic in acid mine drainage by GFAAS

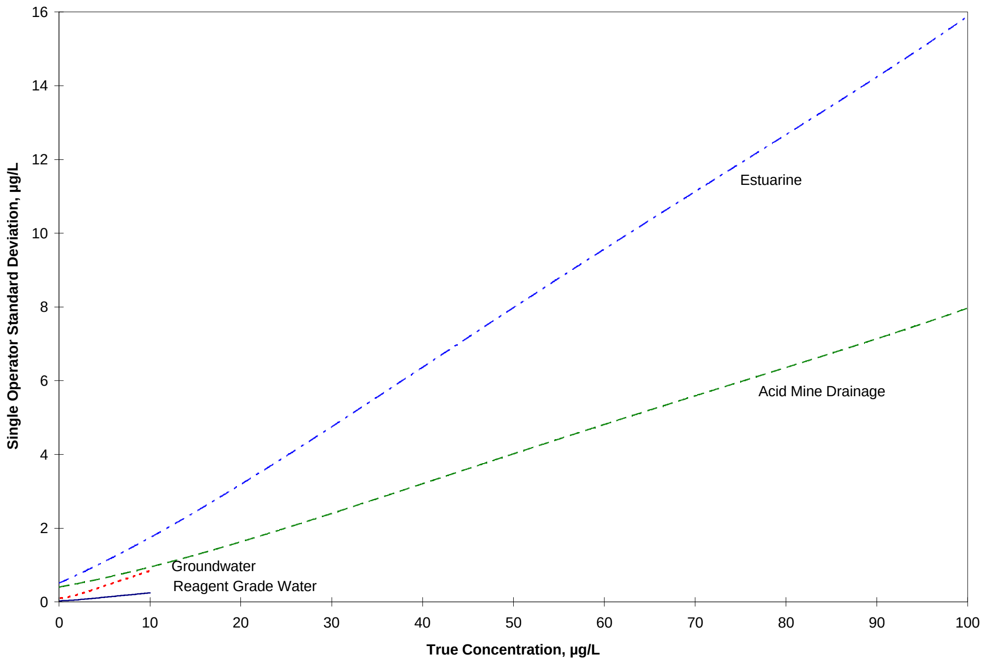


Figure 7-13 Plot of the single operator standard deviation versus the true concentration for cadmium by GFAAS

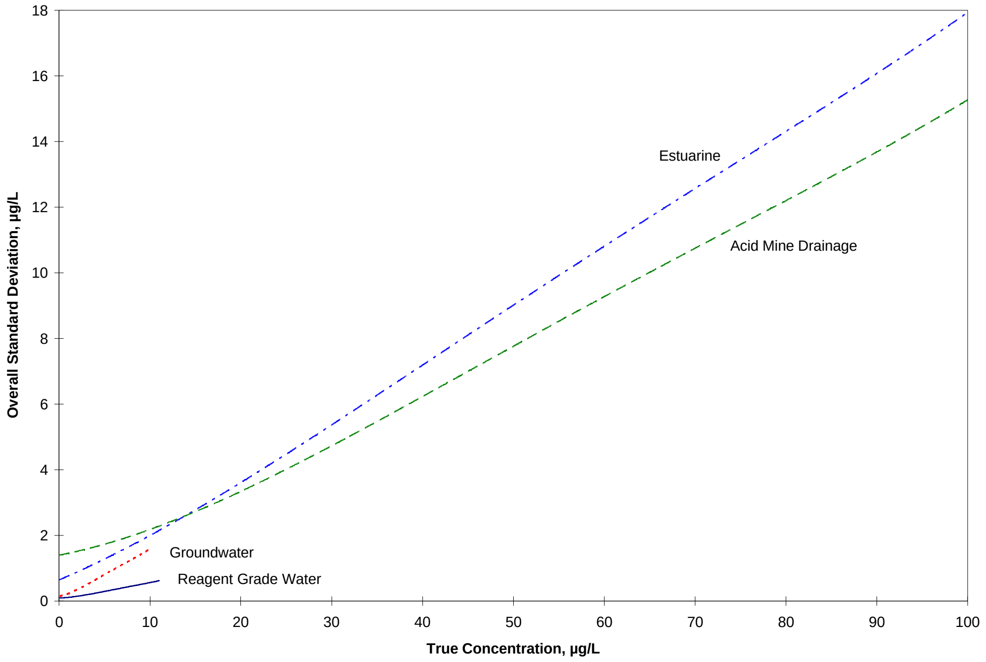


Figure 7-14 Plot of the overall standard deviation versus the true concentration for cadmium by GFAAS

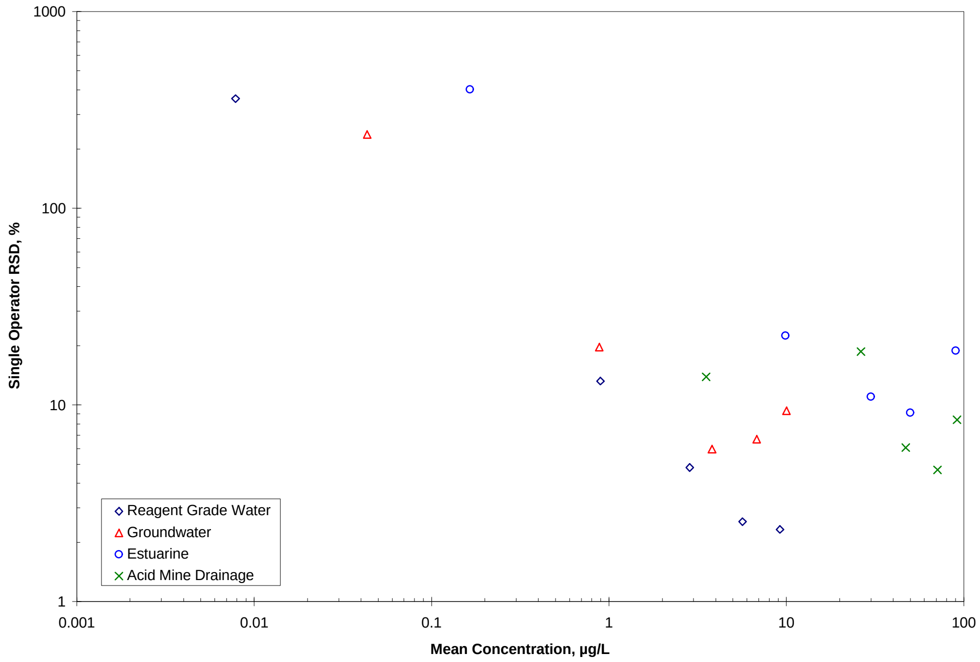


Figure 7-15 Plot of the single operator relative standard deviation versus the mean concentration for cadmium by GFAAS

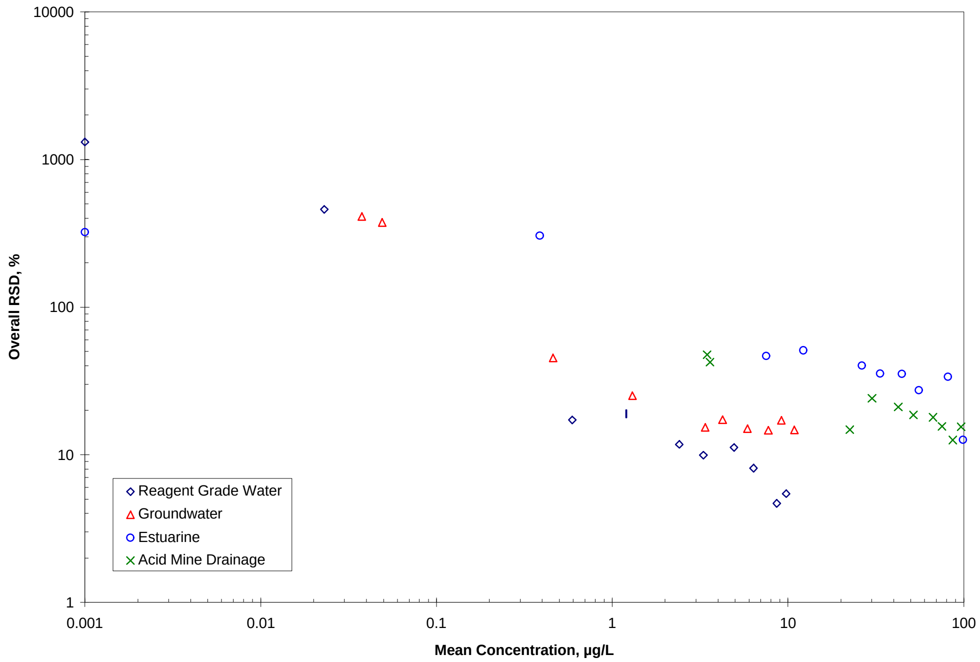


Figure 7-16 Plot of the overall relative standard deviation versus the mean concentration for cadmium by GFAAS

Cadmium Recovery. Figure 7-17 is the plot of the recovery (mean result versus true concentration) for cadmium in all matrices. Some recoveries for estuarine and acid mine drainage were beyond the 90 to 110% percent recovery range, but all recoveries were within 80 to 120%. Figures 7-18 through 7-21, recovery plots by matrix with the weighted linear regression shown, illustrate good linearity of the recovery data with the recoveries trending a bit high for reagent grade water, groundwater and acid mine drainage. The estuarine recoveries were fairly linear but trended low at the lower concentrations.

7.3.3 *Chromium*

Chromium Standard Deviation. Figure 7-22 shows the single operator standard deviation versus true concentration of chromium for all matrices. The single operator regression curves are similar for all matrices across the concentration ranges studied. Figure 7-23, the overall standard deviation plot, shows that the higher TDS matrices, estuarine and acid mine drainage, have higher absolute standard deviations than the lower TDS matrices, reagent grade water and groundwater. Absolute standard deviations were highest for acid mine drainage above approximately 50 µg/L.

Figures 7-24 and 7-25 plot the single operator and overall relative standard deviation versus mean concentration for all matrices using a log/log scale. A general trend of decreasing RSD with increasing concentration is observed, leveling off at less than about 10% for single operator RSDs and 20% for overall RSD.

Chromium Recovery. The recoveries (mean results versus true concentrations) for chromium in all matrices, plotted in Figure 7-26, were within ±10%. The plots by individual matrix, Figures 7-27 through 7-30, illustrate the good recoveries for each matrix.

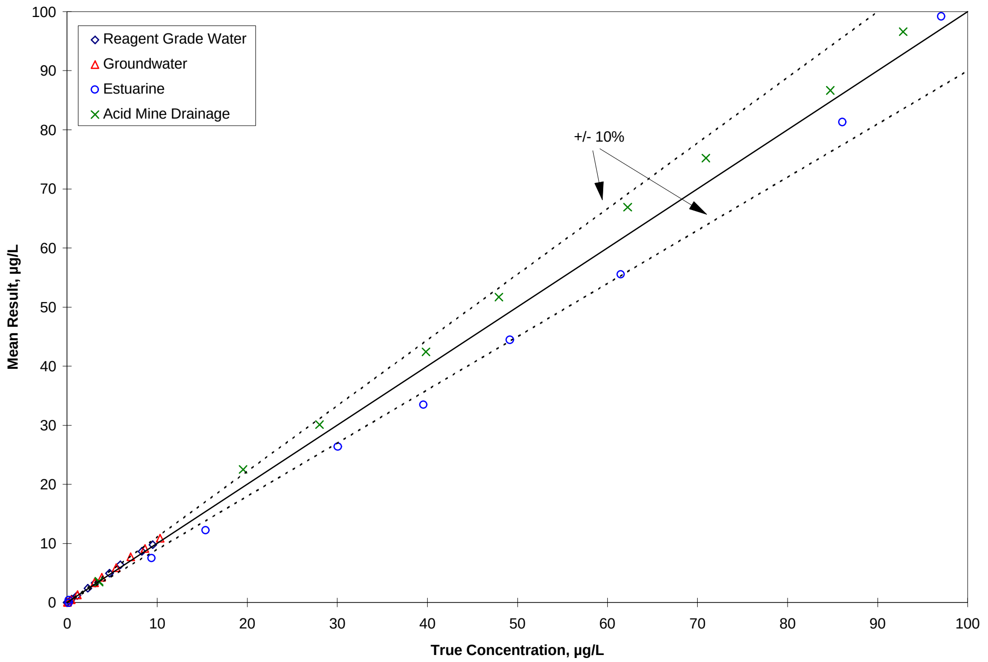


Figure 7-17 Plot of the mean result versus the true concentration for cadmium in all matrices by GFAAS

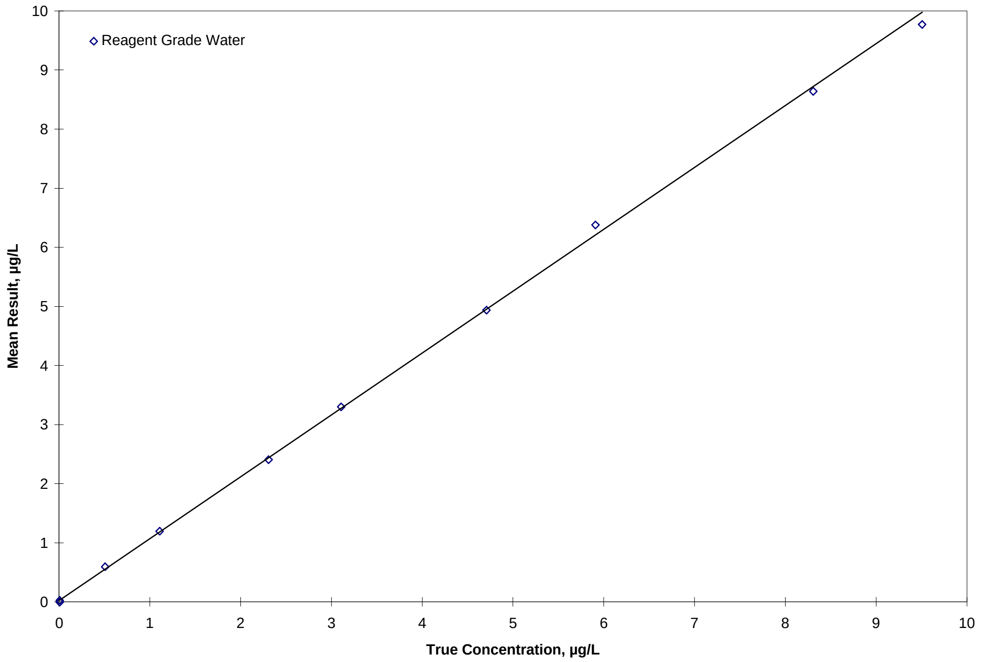


Figure 7-18 Plot of the mean result versus the true concentration for cadmium in reagent grade water by GFAAS

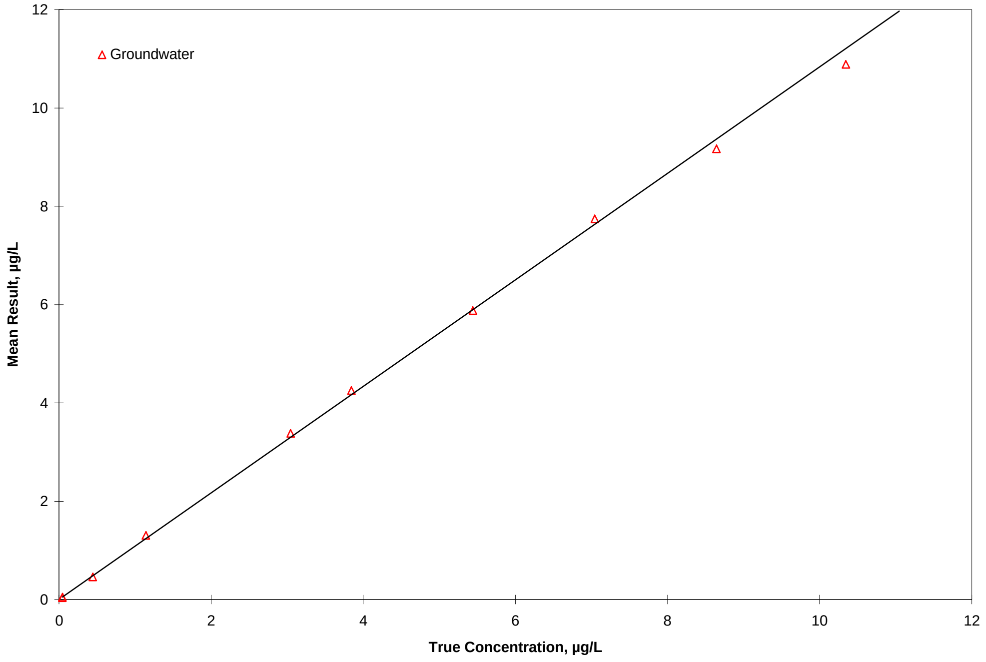


Figure 7-19 Plot of the mean result versus the true concentration for cadmium in groundwater by GFAAS

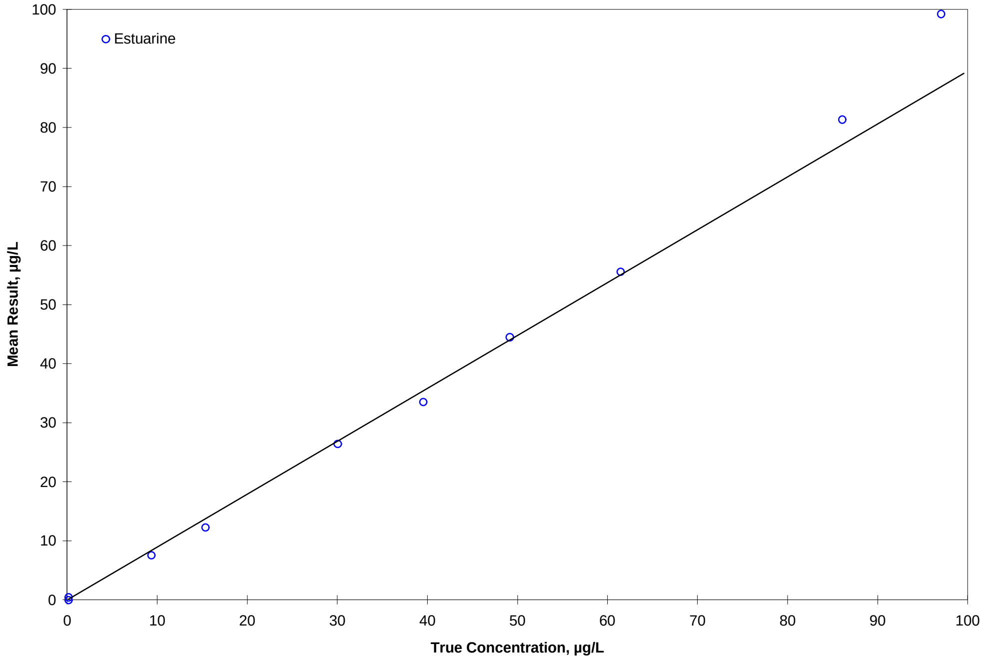


Figure 7-20 Plot of the mean result versus the true concentration for cadmium in estuarine water by GFAAS

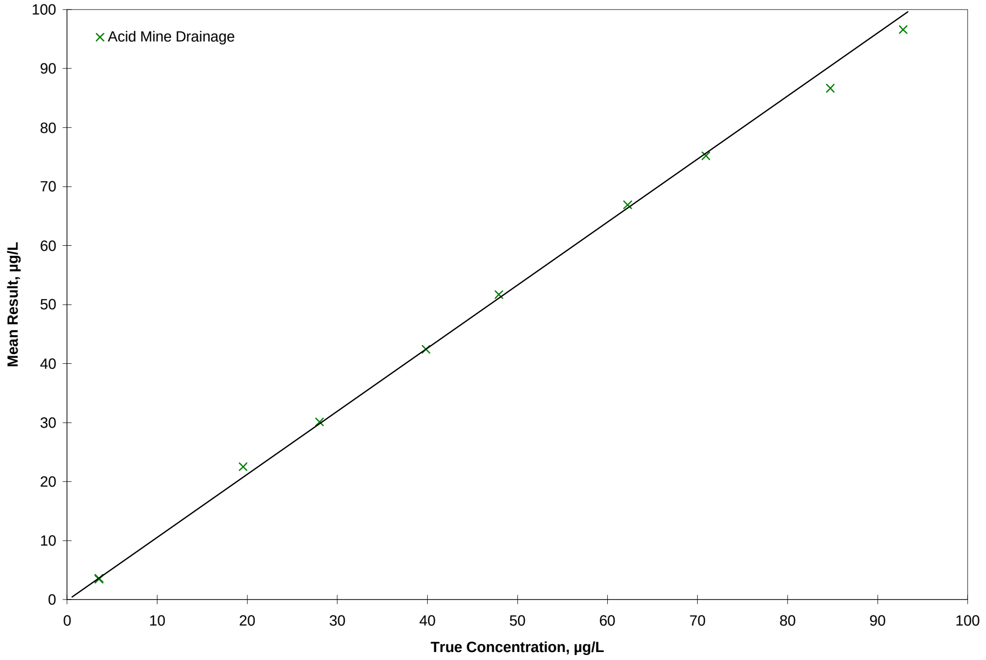


Figure 7-21 Plot of the mean result versus the true concentration for cadmium in acid mine drainage by GFAAS

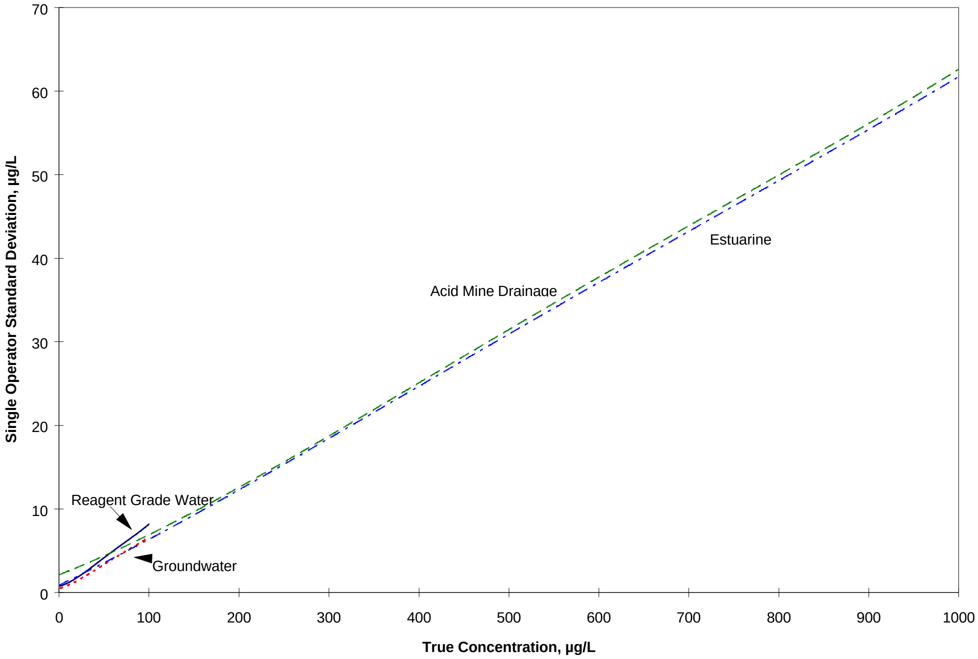


Figure 7-22 Plot of the single operator standard deviation versus the true concentration for chromium by GFAAS

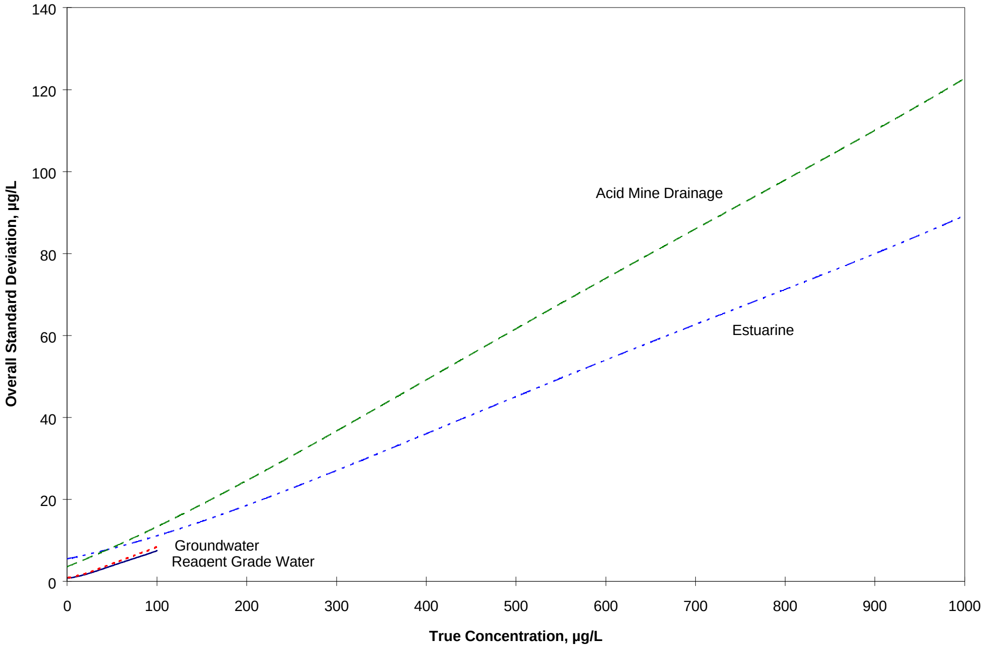


Figure 7-23 Plot of the overall standard deviation versus the true concentration for chromium by GFAAS

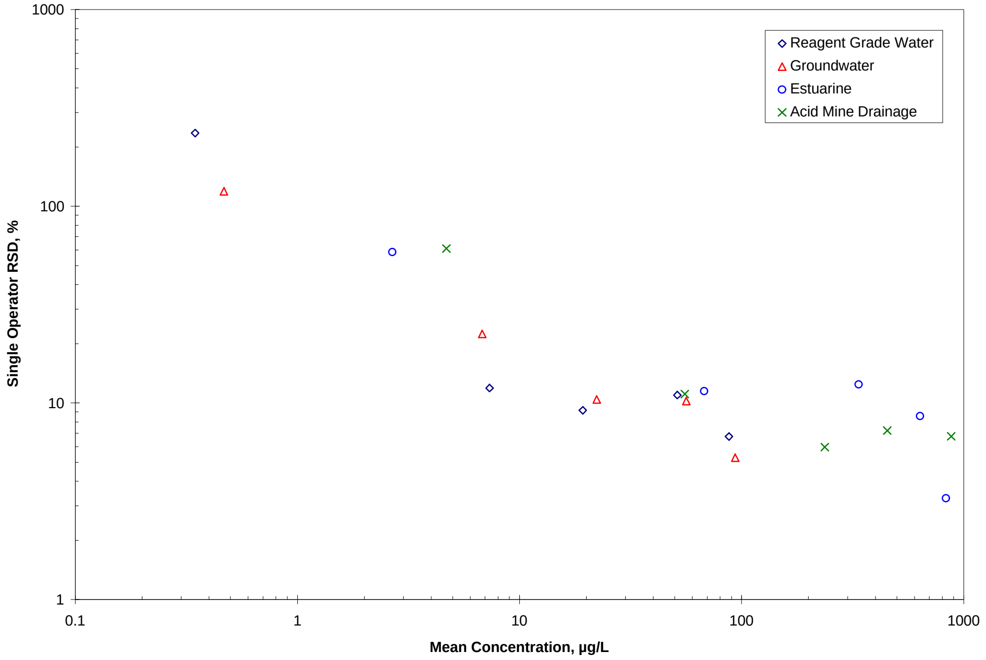


Figure 7-24 Plot of the single operator relative standard deviation versus the mean concentration for chromium by GFAAS

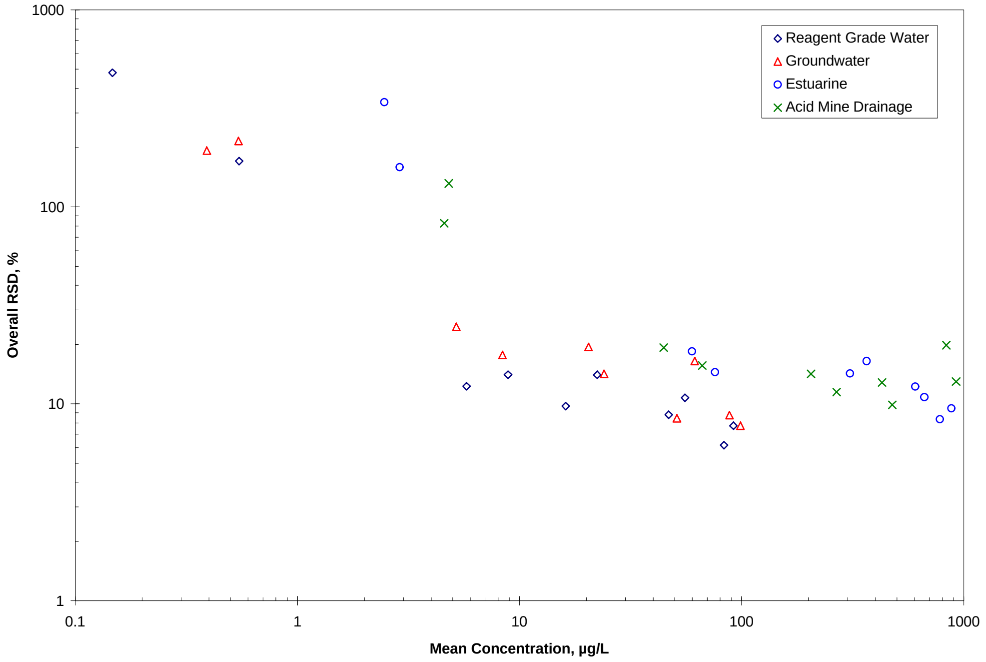


Figure 7-25 Plot of the overall relative standard deviation versus the mean concentration for chromium by GFAAS

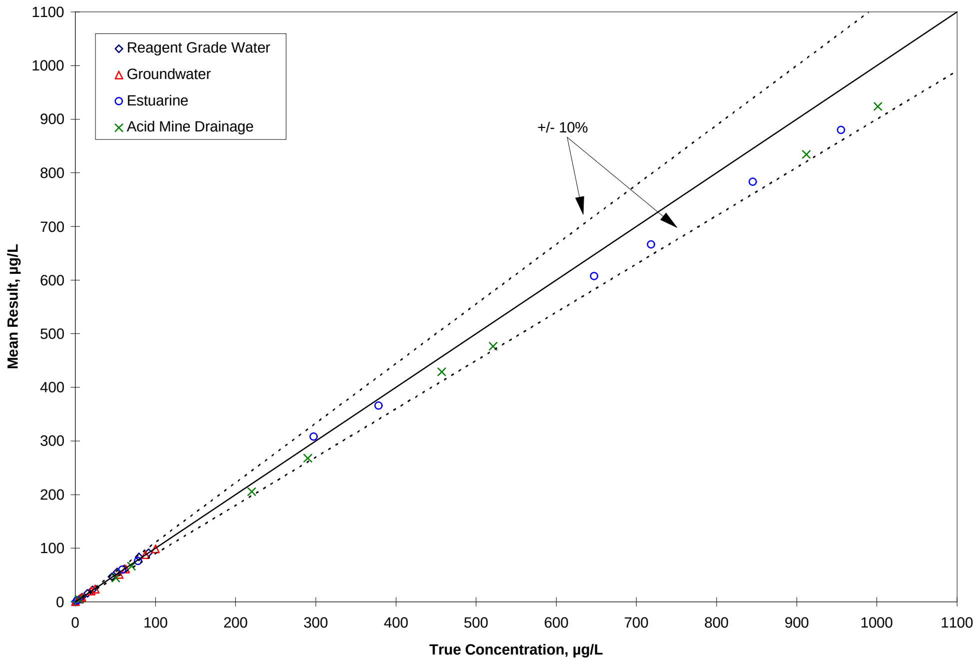


Figure 7-26 Plot of the mean result versus the true concentration for chromium in all matrices by GFAAS

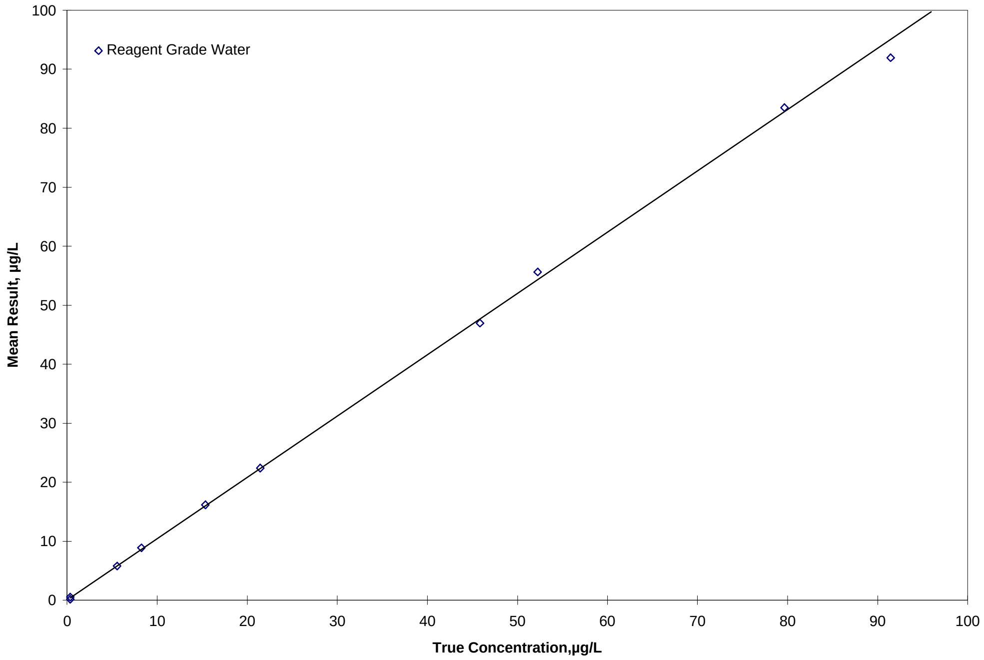


Figure 7-27 Plot of the mean result versus the true concentration for chromium in reagent grade water by GFAAS

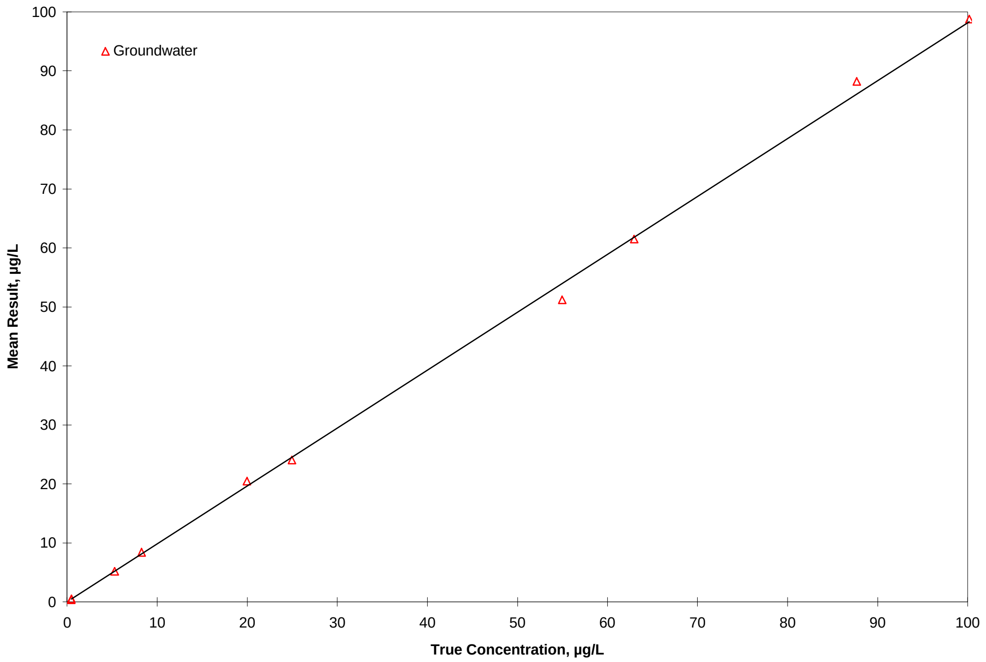


Figure 7-28 Plot of the mean result versus the true concentration for chromium in groundwater by GFAAS

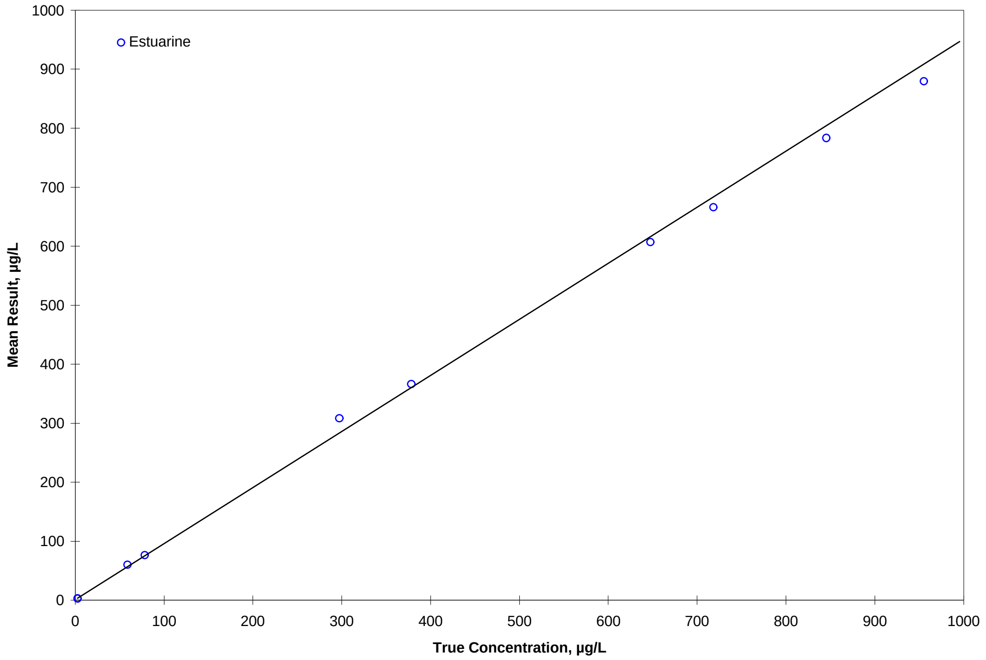


Figure 7-29 Plot of the mean result versus the true concentration for chromium in estuarine water by GFAAS

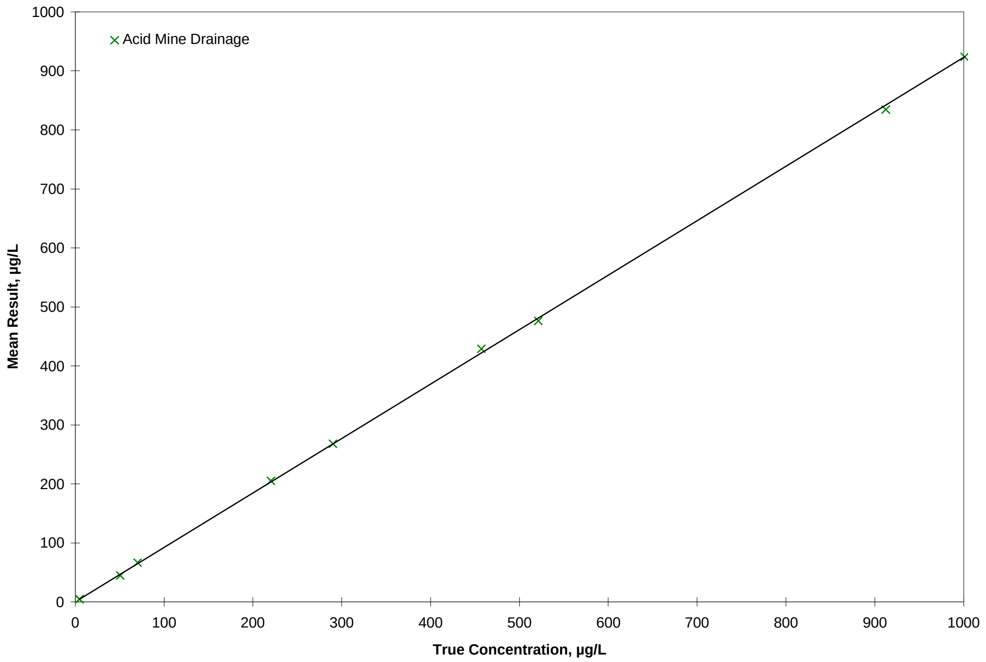


Figure 7-30 Plot of the mean result versus the true concentration for chromium in acid mine drainage

7.4 References

1. American Society for Testing and Materials, "Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water," D2777-96, *Annual Book of ASTM Standards*, 1997.

8

ALTERNATIVE MINIMUM LEVEL

In order to evaluate and negotiate permit levels, utilities require detection and quantification level definitions and values that specifically address compliance monitoring situations by incorporating the following:

- Interlaboratory standard deviation to account for the variability associated with the analysis of split samples by the utility and the regulator, and the use of different laboratories over the life of the permit
- Estimates of the standard deviation over a range of concentrations including zero, if possible, to account for changes in standard deviation with concentration
- Terms and definitions readily discernible by users as different from existing definitions based on single-operator or pooled single-operator standard deviation
- Statistical treatment of data appropriate for future monitoring decisions.

In the 1994 draft EPA guidance (1) for dealing with detection and quantification levels in the National Pollutant Discharge Elimination System (NPDES) for setting and determining compliance with water quality-based effluent limitations (WQBEL), when measured data are below the quantification level the USEPA proposed that:

- Zero would be used in place of all analytical results below the quantification level
- Quantification would be computed using the interim Minimum Level (ML).

Setting the quantification level at the interim ML, as the USEPA proposes to define it, is not justified for a number of technical reasons. This section will explain the technical and regulatory issues behind the selection of a quantification level and will provide the background for the approach recommended by EPRI to compute a quantification level that can be used in the compliance monitoring environment.

Section 8.1 describes the fundamentals of detection and quantification levels using terminology based on the commonly accepted convention by Currie (2, 3). In Section 8.2, we briefly summarize several of the key approaches suggested for defining detection and quantification levels that have been considered to date. Also in Section 8.2 the shortcomings with the USEPA 40 CFR Part 136 Method Detection Limit (MDL) and EPA's proposed interim Minimum Level (ML) definitions for detection and quantification, respectively, are documented. During 1995, EPRI participated in an industry coalition that developed a technical consensus on principles and properties associated with detection and quantification. As a result, a statistically defensible estimate of a quantification level called the Alternative Minimum Level (AML) was developed. In Section 8.3 the problems and proposed solutions to modeling standard deviation data are illustrated using data developed from this EPRI project. Section 8.4 presents the Alternative Minimum Level (AML), and explains how the AML relates to the earlier Compliance Monitoring Detection Level (CMDL) and Compliance Monitoring Quantitation Level (CMQL) definitions published by EPRI. Section 8.4 also shows how the AML addresses the problems with the interim ML and presents the procedure for computing the AML using the interlaboratory data from this validation program. In Section 8.5 the reader is provided guidance on the use of the data in this report in the context of compliance monitoring permits. The ASTM Interlaboratory Detection Estimate (IDE) is introduced in Section 8.6.

8.1 Technical Approaches to Detection and Quantification Levels for Demonstrating Regulatory Compliance

There are a myriad of terms for levels of detection (e.g., Method Detection Limit (MDL), Detection Level (DL), Instrument Detection Level (IDL)), but their conceptual foundations are often quite diverse leading to inconsistency in practice. Although less intensively studied, the same problem exists for limits of quantification (4). Over the years chemists have used "2-sigma" and "3-sigma" detection levels without precise definition or meaning. The United States Environmental Protection Agency (USEPA) continued this practice when they published detection levels (DL) without definition in the Methods of Chemical Analysis of Water and Wastes (MCAW) (5). Unfortunately, these levels have been widely used in the regulatory environment, where they were neither intended nor appropriate, because levels specific to compliance monitoring had not been introduced (6,7). To provide a framework within which to compare and contrast these various methodologies, the pioneering work of Currie (2) is used.

8.1.1 *The Detection Problem*

With respect to analytical detection, Currie (2) defined two levels; the critical level (L_C) and the detection level (L_D). The L_C is the point at which "one may decide whether or not the result of an analysis indicates detection." The L_D is the point at which "a given analytical procedure may be relied upon to lead to a detection." There is an important distinction between these two levels. At the L_C we have confidence that a measurement is not a “false positive.” We are minimizing the chance of erroneously reporting that something is present when it is not. However we must go up to the detection level before we can be confident that the analytical procedure is not “missing” a substance when it is actually present. At the L_D we are confident that a measurement is not a “false negative” or a “false positive.”

Statistically, the L_C is the concentration above which the response signal is significantly different from zero (Figure 8-1). When a measurement exceeds L_C, we can make the binary decision, "detected." A measured result at or above the critical level tells us the pollutant is present. But a measured result below the critical level does not tell us with confidence that the pollutant is absent. That is because replicate measurements of a sample with a true value equal to the critical level will fall both above and below the critical level at roughly the same frequency.

Those measured results falling below the critical level will be deemed non-detects. But those measured results really are false non-detects, given that the true value is equal to the critical level (and thus we know the pollutant is present). Note that when the "true" concentration is zero, the probability of the correct decision "not detected" is $(1 - \alpha)$ where α is the Type I error rate or false positive rate of the statistical test. The Currie L_C is equivalent in concept to the EPRI Compliance Monitoring Detection Level (CMDL) developed in an earlier effort (7).

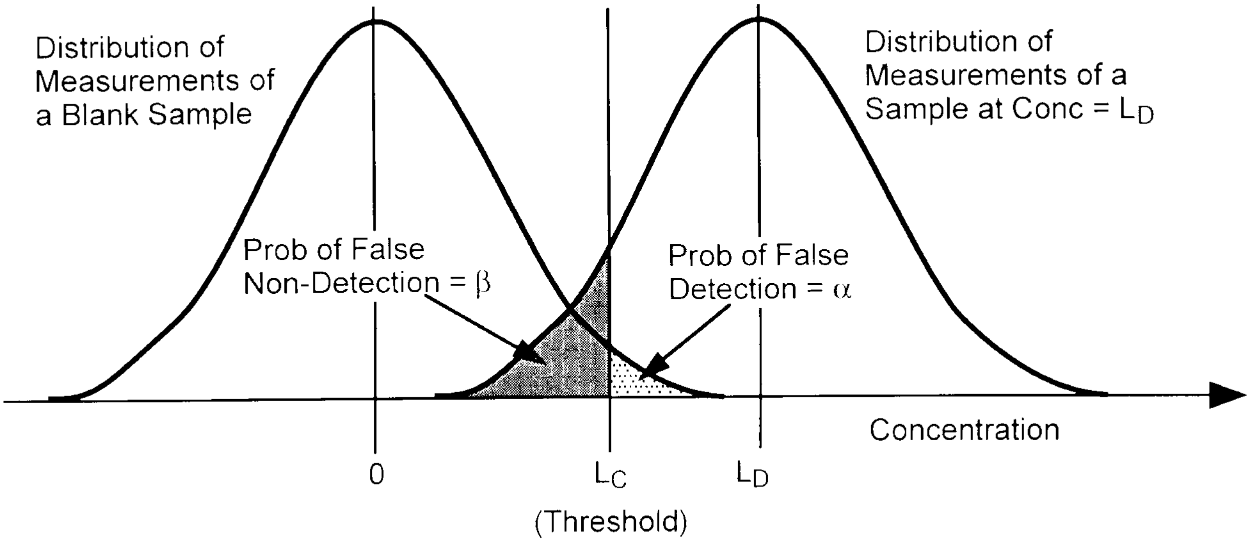


Figure 8-31 Relationship between Currie's L_C and L_D.

Assuming a symmetric distribution of measurement errors, when the "true" concentration is equal to L_C the probability of reporting it below L_C is 50%. This is termed the Type II error rate or false negative rate (β).

To accommodate both Type I and II errors Currie developed the "detection level" L_D. At the detection level, the non-detect problem is controlled. While replicate measurements of a sample with a true value equal to the L_D will fall both above and below the L_D, the detection level has been developed to ensure that virtually all of the measurements falling below it will nonetheless fall above the L_C. Thus, for a true value equal to the L_D, virtually all of the measurements that fall below the L_D will be deemed detected. Only a very small set percentage (e.g., 1 %) of those measurements will fall below the critical level and be deemed erroneously non-detects.

When the true concentration is L_D, then the Type II error rate (β) using L_C as the critical level is small. For example, assuming that $\alpha = \beta = 0.01$, then another way of stating this is that 99 % of the measured concentrations for samples not containing the analyte will be less than the L_C and 99% of the measured concentrations for samples with true concentration equal to L_D will be greater than L_C. That is, when the true concentration is equal to the L_D, the probability of a measurement below the L_C is 1% (2). Currie's L_D definition is conceptually equivalent to the EPRI Compliance Monitoring Quantitation Level (CMQL) developed in earlier efforts (7). It should be noted that Currie did not specify the source of data variability whether from within lab or between lab errors.

As can be seen from these definitions, the critical level and detection level are quite distinct. Above the critical level, we can have (1 - α) 100% confidence that the true concentration is greater than zero; whereas above the detection level we can have (1 - β) 100% confidence that the true concentration is greater than L_C. Figure 8-1 illustrates the relationship between L_C and L_D and Table 8-1 summarizes the definition and implications of the Currie scheme for defining detection and quantification levels. A number of other authors have followed Currie's lead and proposed definitions for detection and quantification levels to include control of both false positive and false negative rates (8, 9, 10, 11, 12, 13).

8.1.2 *The Quantification Problem*

Currie (2) defined the determination level (L_Q) as the concentration "at which a given procedure will be sufficiently precise to yield a satisfactory quantitative estimate." This definition is similar to that used by Adams, Passmore and Campbell (14) who defined a "minimum working concentration" as that for which the relative standard deviation (RSD) was 10%. The American Chemical Society (ACS) (11) chose to define quantification as the lowest concentration at which a ± 10% relative standard deviation (RSD) could be obtained. The determination level has since been described by several names, most notably "Practical Quantitation Level" PQL (15) and "Limit of Quantitation" (16). USEPA (16) defines the PQL as "the lowest level achievable by good laboratories within specified limits during routine laboratory operating conditions." The USEPA has also defined the quantification level over the years in at least two ways: (1) as 5 or 10 times the method detection limit (MDL), and (2) as the lowest true concentration at which 75 % of the laboratories in an interlaboratory study can measure within the "acceptance limits." The first definition is arbitrary, and depends completely on the validity of the corresponding method detection limit, about which serious questions have already been raised (17). The second definition is considerably better; however, the interlaboratory studies are often done in experienced government laboratories that "knew they were being tested with standard samples in distilled water without matrix interferences." The USEPA (15) also points out that, "Actual day-to-day operations in a wide variety of laboratories using real samples in natural water would be expected to produce poorer results, i.e., wider performance ranges especially at the lower concentration levels."

Table 8-1

Summary of Currie's(2) Scheme for Detection and Quantification Levels

Level	Definition	Statistical Implications
Critical level, L_C	“The point at which one may decide whether or not the result of an analysis indicates detection.”	False positive (Type I) error rate controlled; signal is statistically different from zero. Equivalent to the EPRI CMDL.
Detection level, L_D	“The point at which a given analytical procedure may be relied upon to lead to a detection."	False positive and false negative (Type II) error rate controlled; essentially the definition of the EPRI CMQL
Quantification level, L_Q	“The concentration at which a given procedure will be sufficiently precise to yield a satisfactory quantitative estimate.”	Lowest concentration at which an RSD of 10% obtained.

Kempic of the USEPA presented detailed procedures (18) using interlaboratory studies for calculating acceptance limits (ACL) and the practical quantitation level (PQL) which the USEPA (19) defined as the lowest true concentration for which greater than 75% of the laboratories can measure within ± the ACL. The latter was based on the 95% confidence limit at the maximum contaminant level goal (MCLG) or, where the MCLG was zero, at a concentration five times the Method Detection Limit. Britton (20) of the USEPA proposed an alternative definition for LOQ - the lowest true concentration for which the probability of an analytical response below the detection level is small. This definition was similar to one proposed earlier by Currie (2). It is important to note that the ACS definition, the USEPA definition of PQL as a multiple of the MDL, as well as the above Britton alternative utilize only intralaboratory standard deviation for their derivation. (See Koorse (21) for a review of the legal implications of these definitions.)

8.1.3 *Calibration Curve Methods for Computing Detection and Quantification Levels*

In recent years, a great deal of interest has been shown in the use of "calibration curve" procedures to compute the two fundamental detection parameters defined by Currie: his critical level (L_C) and his detection level (L_D). Some prescribed procedure is followed using replicate samples at multiple levels of known concentration (but in almost all instances, the replicate samples are not externally prepared reference samples), to produce a set of points of measured (observed) concentration vs. actual (true) concentration. Some form of linear or other regression on this set of points is then performed to produce the curve of actual vs. measured concentration, known as the "Calibration Curve." An uncertainty interval around the curve is then calculated. All of the calibration curve methodologies follow the above basic procedure: it is in the details of the type of regression (ordinary least squares, weighted least squares, curvilinear, etc.) and the type of uncertainty interval (prediction or tolerance intervals) that the various methods differ. Once generated, this calibration graph or expression can be readily applied to determine the two fundamental detection parameters defined by Currie. Included in this class are methods by Hubaux and Vos (22), Clayton, et al. (23) USATHAMA (24), Gibbons, et al. (25), Coleman (26).

8.2 EPA Definitions of Detection and Quantification and Their Problems

The concept for the Method Detection Limit (MDL) was proposed in 1981 by Glaser et al. (12). The proposed approach computed a detection level based on the standard deviation of replicate measurements at a single concentration combined with a hypothesis test (at the 0.99 level) to determine a quantity similar to the critical level defined by Currie (2). The method (13) currently applied by EPA in 40 CFR Part 136 closely follows the method of Glaser (12). For a particular sample analyte, n replicate analyses (minimum of 7) are performed at a single spiking concentration. All n replications typically are performed at the same laboratory. Based on the standard deviation(s) of these n measurements, a Currie L_C type parameter (which EPA calls the "Method Detection Limit" (MDL)) is calculated as:

$$MDL = t_{(0.01,n-1)} \cdot s \qquad \text{(eq. 102)}$$

where t is the appropriate value from the t-distribution for n-1.

The EPA's current estimate of a limit resembling a quantification level is based loosely on the "Limit of Quantitation (LOQ)" defined by the American Chemical Society (9) as the lowest concentration with an RSD of 10% (i.e., the ratio of measurement standard deviation to measurement mean concentration = 0.1 or, the measurement mean is ten times the standard deviation). While the ACS and Currie have also expressed the quantification level (L_Q) as a "10 sigma" limit, their sigma actually refers to the standard deviation of a net signal or concentration and not the true population standard deviation. If one assumes the "sigma" to be constant versus concentration, the 10 sigma quantification level can be shown to give an RSD of 10% because:

$$RSD = \left(\frac{s}{L_Q} \right) \times 100\% \qquad \text{(eq. 103)}$$

$$RSD = \left(\frac{s}{10s} \right) \times 100\% \qquad \text{(eq. 104)}$$

$$RSD = (0.10) \times 100\% \qquad \text{(eq. 105)}$$

or

$$RSD = 10\% \qquad \text{(eq. 106)}$$

The EPA interim Minimum Level (ML), described on page 8-1, was derived from the "10 sigma" definition by assuming that the standard deviation at the MDL and the interim ML are the same hence:

$$MDL = 3.14s \qquad \text{(eq. 107)}$$

and

$$ML \cong 10s \qquad \text{(eq. 108)}$$

so

$$\frac{ML}{MDL} = \frac{10s}{3.14s} = 3.18 \qquad \text{(eq. 109)}$$

thus:

$$ML \cong 3.18 \times MDL \qquad \text{(eq. 110)}$$

In the compliance monitoring situation, there are a number of problems with EPA's approach to computing an interim ML. The EPA draft guidance (1) directs that an interim ML be developed by multiplying the published MDL by 3.18 and then rounding "to the nearest multiple of 1, 2, 5, 10, 20, 50 etc." Yet by EPA's definition, the interim ML is supposed to represent the lowest value that can be reliably quantified. If the calculated value for the interim ML is rounded down, the resulting value will fall below the level that EPA deems to be quantifiable.

The biggest problem with the interim ML is that it is nothing more than a multiple of the MDL, which itself is a flawed statistic for a number of reasons:

- MDLs are based on intralaboratory data - Compliance monitoring is an interlaboratory comparison between the permittee and the permitter, yet the MDL can be based on only one analyst in one lab performing the MDL analysis in reagent grade water. Table 8-2 developed from EPRI RP1851 and EPA Method Study data, shows that the ratio of interlaboratory (s_t) to intralaboratory (s_o) precision (pooled single operator)varies from 1.2 to 2.5.
- The MDL is not reproducible - The EPA specifically states in 40 CFR Part 136, Appendix B that MDLs "are not necessarily reproducible on a routine basis in a given laboratory, even when the same analytical procedures, instrumentation and sample matrix are used." What this means in practice is that an MDL computed from day to day or analyst to analyst will vary. A statistic with this sort of problem is not a good way to assess the ability of a method to measure analytes at or below the water quality based effluent limits (WQBEL).
- MDLs assume constant variance - The implicit EPA model of the MDL assumes that the standard deviation at zero is the same as that at the MDL. However, since variance is not constant with concentration, the MDL will be highly dependent on the spiking concentration. The lower the spike concentration the lower the MDL will be. In effect the MDL is not anchored statistically. If the MDL is to be determined in reagent grade water, 40 CFR Part 136 recommends that the test concentration be within a factor of 1 to 5 times the estimated MDL in reagent grade water. For a sample, if the analyte concentration does not exceed 10 times the estimated MDL in reagent grade water, the sample may be used as is for the determination of the MDL. Since the spiking concentration can vary over a wide range, the computed MDL can vary over that range. Figure 8-2 illustrates the point. Using the data from previous RP1851 validation studies, an MDL was computed at various spike ratios that were in the prescribed range stated in 40 CFR Part 136, Appendix B. As Figure 8-2 shows, the MDL varies by over a factor of 2.5 in this example. There are other examples where the spike to MDL levels off below 5:1, so that essentially any estimate of the MDL over some minimum concentration range would be valid.
- MDLs are not statistical predictors of laboratory performance - MDLs are based on the t-statistic which establishes a distribution of parameter estimates. It is not meant to predict multiple future events. The Alternative Minimum Level (AML) uses the

tolerance statistic which predicts a percentage of multiple future measurements with a desired level of confidence in the computation of a quantification level.

- In the published 40 CFR Part 136 methods, some MDLs have been listed, but no supporting data have been published with the methods.

Table 8-2

Summary of Representative Ratios of Interlaboratory to Intralaboratory Standard Deviation.

Method	s_t/s_o
Organic Pollutants	
MS-24, Method 601	2.2
MS-14, Method 604	2.3
MS-18, Method 608	1.2
MS-20, Method 610	1.5
NCASI, Method 1653	2.1
Metal Pollutants	
MS-31, 200 Series GFAAS	1.5
AWWA, 200.9 STPGFAAS	1.6
EPRI, 200 Series GFAAS	2.5

s_t - Interlaboratory standard deviation

s_o - Intralaboratory (pooled single operator) standard deviation

For a more complete discussion of the issues and problems associated with the interim ML (and MDL), the reader is directed to Koorse (27).

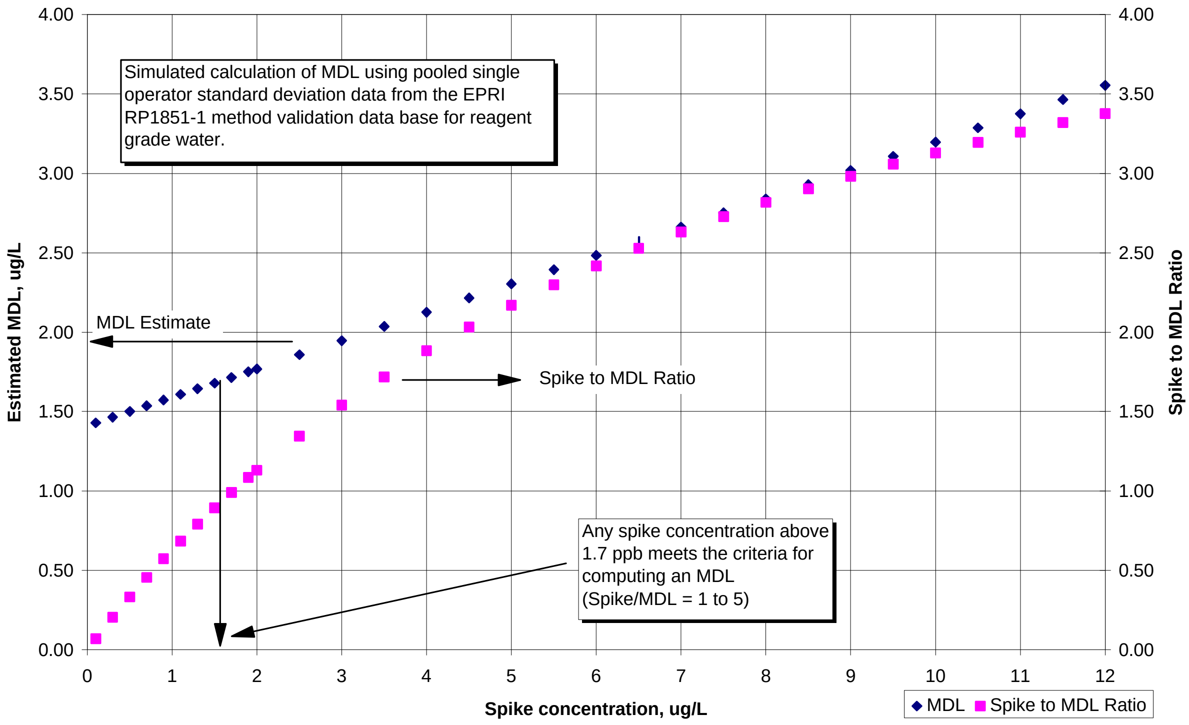


Figure 8-2. Effect of Changing the Spike Concentration on the Computation of the EPA MDL in Reagent Grade Water for Selenium by GFAAS

8.3 Modeling Standard Deviation Data

The original EPRI model for the behavior of standard deviation postulated that at or below the critical level the standard deviation would be nearly constant, primarily influenced by instrument noise. At some concentration the standard deviation would start to increase and eventually be proportional to the true concentration. Initially a linear equation was fitted to the standard deviation versus true data under the assumption that all the test concentrations were close to the detection limit. However, plots of the data and occasional negative intercepts indicated that our assumption was incorrect. To compensate for the curvature in the data sets, the data were fitted subsequently to an expression in the form:

$$s_t = a_0 a_1^{\;T} \qquad \text{(eq. 111)}$$

or

$$s_t = a_0 e^{a_1 T} \qquad \text{(eq. 112)}$$

where s_t is the interlaboratory standard deviation (as defined by ASTM D2777). Figure 8-3 shows the precision data from all of the EPRI GFAAS tests for the RGW, RW and APO matrices (note: the x-axis is logarithmic to accentuate the low concentrations). The exponential fit is reasonable and conceptually provides a relationship consistent with chemical laboratory observations.

Recently, Rocke and Lorenzato (28) suggested a model that appears to reflect the "hockey stick" form of the relationship between standard deviation and the true concentration. The Rocke-Lorenzato (R-L) equation can be simplified to the form:

$$s_t = \left(a_0 + a_1 T^2\right)^{1/2} \qquad \text{(eq. 113)}$$

This model is based on the assumption that the variance is composed principally of two error terms: 1) errors that are unrelated to analyte concentration (e.g. ambient contamination) and 2) errors that are proportional to analyte concentration (e.g. nebulizer flow variability).

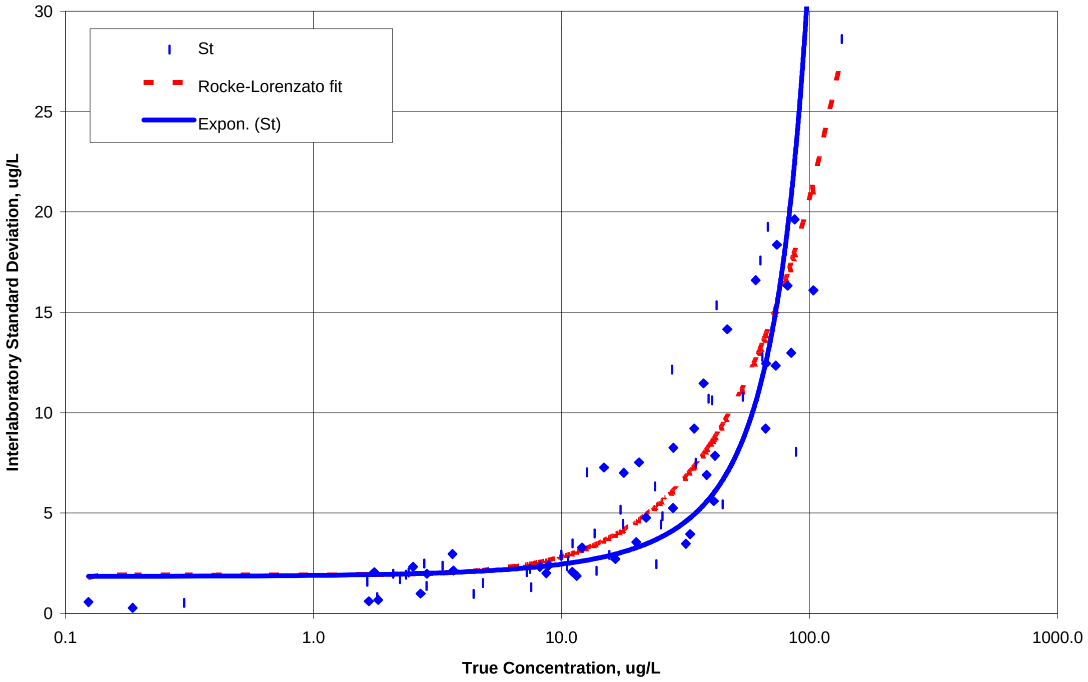


Figure 8-3. Curvilinear relationship of Interlaboratory Standard Deviation versus True Concentration; EPRI GFAAS Data for RGW, RW and APO.

Looking at Figure 8-3, both the exponential and the R-L models do a reasonable job at fitting the data to the lower concentrations, but the R-L model has a much better fit to the data above 10 μg/L (this point is very apparent when the x-axis is a linear scale).

8.4 Alternative Minimum Level

During the summer of 1995, EPRI along with the Inter-Industry Analytical Group (IIAG), an industry coalition, conducted an extensive review of available detection and quantification level definitions (27). This evaluation produced two major outputs:

- A list of properties and performance standards to evaluate detection and quantification level definitions, and
- A consensus agreement on an Alternative Minimum Level (AML) to estimate a method's quantification level.

An evaluation of the original Compliance Monitoring Detection Level (CMDL) and Compliance Monitoring Quantitation Level (CMQL) definitions against the list of properties and performance standards for detection and quantification levels indicated that improvements were necessary to explicitly incorporate the dependence of quantification on relative standard deviation. Working within the industry coalition, EPRI developed a definition called the Alternative Minimum Level (AML) based on the CMDL and CMQL, but with additional statistical improvements to address relative standard deviation requirements. The following sections provide the background and computational approach to the AML.

8.4.1 *Background and Overview*

To address the problems identified with the MDL and the standard deviation data (single operator, single concentration) used to compute it, EPRI (7) originally developed the concept of the CMDL. The CMDL addressed the need for an interlaboratory based estimate of a detection level directed at the compliance monitoring case where the discharge permit was set at no permissible discharge (zero) of the regulated pollutant. In that situation the EPRI CMDL was equivalent to the concept behind Currie's (2) critical level (L_C) (which is simply the lowest concentration that is distinct from zero to a specific level of confidence, thereby avoiding false positive errors). In EPRI's case, the CMDL was computed from the interlaboratory precision data from round robin validation studies with 20-30 laboratories and expressed as a curvilinear regression equation. A tolerance statistic was used to make the defined limit suitable for future measurements rather than the t-statistic used by the EPA, which is only meant to describe an existing population. This change in the computational process (7) addressed the problems described above with the MDL, but did not fully bring the CMDL to an estimate of a detection level under Currie's definition. The CMDL, however, may still be valuable possibly in cases where the regulatory limit is set at zero.

In this report L_{CI}, where the subscript "I" refers to interlaboratory to differentiate it from Currie's L_C, will be used in place of the CMDL to provide a direct link to Currie's approach to detection. The L_{CI} is computed in the same fashion as the CMDL was, but the calculation of the degrees of freedom has changed from "n-2" to "n" This change will cause a decrease in the k-factor used to compute the L_{CI} compared with the k factor used for the CMDL; therefore, the L_{CI} will be slightly lower than the CMDL.

Along with the CMDL, EPRI had developed a definition for the CMQL which, as we noted in Section 8.1.1, is conceptually equivalent to Currie's L_D (detection limit). The CMQL provides both false positive (finding the substance present when it not) and false negative (not detecting it when it is present) protection. The CMQL, while not a true measure of the quantification level as defined by Currie, provides a useful measure for non-zero compliance levels that are at or below the CMDL. In those cases we will have at least 99% confidence that the true concentration is greater than the compliance limit if the measured concentration exceeds the CMQL. For the same reasons stated for the CMDL, the L_{DI} will be slightly lower than the CMQL due to the change in degrees of freedom. Thus both the CMDL (L_{CI}) and the CMQL (L_{DI}) may still have a role in compliance monitoring limits under specific conditions, perhaps as benchmarks to test compliance. To confidently know what the actual discharge value is, we must be at or above the quantification level. The AML was developed to provide an estimate of the true quantification level.

In its draft guidance (1) for dealing with detection and quantification levels in the National Pollutant Discharge Elimination System (NPDES), the USEPA proposed the interim ML as the method for calculating quantification levels. The interim ML, as we have shown above, is a "10 sigma" approach to computing a quantification level. The USEPA, however, has not developed a rigorous procedure for calculation, but instead has simply used a factor times the MDL. All the deficiencies associated with the MDL are thus carried over to the interim ML. Furthermore, because the MDL and ML are not based on a calibration design, which would allow estimation of the standard deviation at any concentration, the relative standard deviation at the ML is not known.

The AML is also a "10 sigma" estimate of the quantification level, but with significant computational improvements and statistical rigor to avoid the problems identified with the interim ML. The AML is defined as 10 times the interlaboratory standard deviation (s_{CI}) at the lowest concentration that is differentiable from zero (L_{CI}). The lowest concentration that is differentiable from zero can be statistically determined and, in the EPRI computational approach, it is anchorable, unlike the MDL which is used to compute the interim ML. Once the lowest concentration differentiable from zero is calculated, the standard deviation is computed at that concentration (using the regression expression for standard deviation versus true concentration that is developed from the interlaboratory data) and then multiplied by 10. The final steps in the computation process correct the raw "10s" value for errors in estimating the standard deviation and true concentration. The AML computational approach does not guarantee a specific RSD, but since the standard deviation versus true concentration equation exists, the RSD at the AML can be computed and compared, for example, to a project's data quality objectives. The resulting approach has been presented to the USEPA at a recent public meeting on behalf of a coalition of interested industries (27).

Inherent in the computation of the AML is the use of the interlaboratory standard deviation and recovery data collected for at least five concentrations starting at zero and going to five times the hypothesized AML. The protocol also includes a mechanism to use intralaboratory data (developed within a single laboratory and matrix) to compute an AML where appropriate interlaboratory method validation data are not available.

The approach for calculating AMLs will depend on the availability of data. Ideally, the data used for calculating an AML should be derived from an interlaboratory data base that reflects the matrix (i.e., the chemical characteristics of the sample in which the pollutant of concern is being measured) for the effluent being analyzed. Such matrix-specific data bases already are available for certain industries. Where industry-specific interlaboratory data are not available, and time or other constraints do not allow for those data to be collected, data from an acceptable interlaboratory method study performed on reagent grade water will have to suffice. The USEPA has developed several interlaboratory data bases that could be applied to calculate AMLs.

For many pollutants, however, no acceptable interlaboratory data are available or a site may need to determine a matrix specific AML for their permit. Whether or not industry-specific interlaboratory or intralaboratory data are available, permittees should have the option of seeking a matrix-specific AML, if their particular matrix interferes with the ability of qualified laboratories to perform acceptably at a prior published AML concentration. In most of those cases, intralaboratory data are available or can be readily generated. While the standard deviation data needed to calculate AMLs cannot be obtained directly from intralaboratory data, such data together with adjustment factors to correct for the difference between interlaboratory and single operator pooled standard deviation can be used to estimate the standard deviation for calculating the AML (see Table 8-2 and section 8.4.2 for additional information).

8.4.2 *Computation of the AML from Interlaboratory Data*

Reference 29 describes in detail the development and computation of the AML and includes a diskette containing the AML program. An overview of the approach to compute the AML is given in Figure 8-4 in the form of a summary protocol. The following sections will provide the user with the necessary information to design an interlaboratory test program and compute an AML from the outlier free data set. Appendix B of Reference 29 provides the user with a protocol to compute an AML from intralaboratory replicate data when interlaboratory data are not available. It is expected

A. The AML shall be calculated based on data from one of the following sources in order of priority:

  1. If available, interlaboratory effluent matrix data shall be utilized for effluent-specific AML.
  2. If data in section A.1. are not available, interlaboratory data for laboratory reagent water may be utilized.
  3. If data in section A.1. or A.2. are not available, or are not appropriate, intralaboratory laboratory data for effluent matrix waters may be utilized with an appropriate correction factor to account for the ratio of interlaboratory/intralaboratory standard deviation.
  4. If data in section A.3. are not available, intralaboratory data for laboratory reagent water may be utilized with an appropriate correction factor to account for the ratio of interlaboratory/ intralaboratory standard deviation.

B. If interlaboratory data in A.1. and A.2. are utilized, the AML shall be derived as follows:

  1. Derive recovery data collected for five or more concentrations starting at zero to 5 times the estimated AML from 6 or more laboratories in a blind study.
  2. Process the data using the outlier removal protocols from ASTM D2777 to produce an outlier free data set.
  3. Prepare an input file for the AML program using the outlier free data from step B.2.
  4. Under “Analysis” in the AML program select “Measured Concentration” and “Best Fit” and then select “Run.” Leave the “Screen Outliers” option off as the outliers have already been removed. The program will compute the AML and produce a chart with the L_{CI}, L_{DI}, and the AML.

C. If intralaboratory data in A.3. and A.4. are utilized, the AML shall be derived as follows (see (29) Appendix B for details):

  1. Conduct a blind intralaboratory study. Prepare test samples at five (or more) concentrations (background plus four spikes) with a minimum of five blind replicates at each test concentration (i.e., one analyst prepares the samples and another analyzes the samples as part of their routine laboratory effort) for a total of 25 test samples.
  2. Determine background concentration using the AML program. Prepare an input file for the AML program using the data from step C.1. Under “Analysis” in the AML program select “Measured Concentration,” “Screen Outliers” and “Best Fit” and then select “Run.” The recovery equation from this first iteration of the raw data can be solved for the x-intercept, which is the background concentration in the matrix. Add the background concentration to all the raw data test concentrations.
  3. Submit the corrected data set to the AML program. Under “Analysis” in the AML program select “Measured Concentration,” “Screen Outliers” and “Best Fit” and then select “Run.” The program will compute the AML and produce a chart with the L_{CI}, L_{DI}, and the AML.
  4. Correct the intralaboratory AML to an estimate of the interlaboratory AML by multiplying it by the appropriate interlaboratory/pooled single operator standard deviation correction factor from Table 8-2 or select a factor from the range of values given in Figure B-3 (29).

Figure 8-4 Summary of AML Test Protocol and Computation.

that the user will employ the AML program contained with the AML report (29) to compute the AML. The AML program is a Windows® based program (runs in Windows 3.1 or Win95®) developed by Gibbons (30) that will process outlier free data files or raw test data, compute the regression equation (exponential, R-L or best fit) for standard deviation and recovery and then compute the AML. The AML program will also output a worksheet containing the AML equations in order of solution with the user's data inserted and plots of the standard deviation and recovery data. Application of this program to computing AMLs will be discussed below and the user is directed to the AML User's Guide in Reference 29, Appendix C for details on installation and operation.

8.4.2.1 *Collection of the Interlaboratory Data*

As we have described above, the AML is insensitive to the test concentrations used to compute the AML. However, the user should note that the range of spiking concentrations must be relevant for computing the AML. In general, the user should attempt to cover the range of concentrations from zero through five times the hypothesized AML. Note, however, that if blank samples are used (i.e., concentration equal to zero), approximately 50% of the measured concentrations should be negative. If the instrument censors these negative concentrations (i.e., sets them equal to zero), the estimated AML (or any other estimator including the MDL and interim ML) will be too low since only half of the true variability is observed. If this is the case, the user should configure the instrument to accept and report negative values. In the event that this is not possible, the operator can select the lowest test concentration at which the censoring of data by the instrument will not occur.

The number of laboratories and replicates depends on the source of data.

- For interlaboratory studies a minimum of 6 laboratories remaining after laboratory ranking and outlier testing are required for each level of each matrix/analyte combination. In practice this usually implies that 8-9 labs should participate in the test program to retain 6 labs. Each participant should be sent 5 Youden pair test concentrations (total of 10 samples) in the test matrix/analyte combination as blind samples. In an alternate test design, the central lab in charge of sample preparation can prepare replicate samples at each of the 5 test concentration (at least 3 replicates per test concentration for a total of at least 15 samples). A second alternative approach is to send sufficient volumes of the 5 test samples so that the laboratory can prepare its own replicates. In this latter case, different personnel should prepare and analyze the samples to maintain the blind nature of the test program.
- When only a single laboratory is performing an AML study, a minimum of 5 test concentrations with 5 blind replicates for each level in the test matrices should be run (a total of 25 samples). Additional test concentrations and replicates can be run if the user chooses. These samples must be prepared as blind samples by someone other than the analyst, randomized and spread over several days while labeled and

analyzed as routine samples. See Appendix B (29) for details on the test design and data analysis protocol for estimating the AML from intralaboratory data.

In both cases the samples should be placed in the laboratory as routine samples to accurately reflect the normal variability and bias in the laboratory.

8.4.2.2 *Testing for Outliers in the Data Sets*

All of the data in this report were first processed through EPRI's software program STATCALC (preliminary research grade) to remove laboratories with consistent bias (lab ranking) and individual outliers (described in Section 6). STATCALC is an implementation of ASTM D2777. Reference 31 describes in detail the D2777 lab ranking and outlier rejection protocol and the procedure was summarized in Section 6. The user can choose to implement the D2777 protocol manually or assisted by a spreadsheet program of their design. They may also request a copy of STATCALC from EPRI by contacting the EPRI Project Manager, Dr. Babu Nott.

For interlaboratory studies we recommend that the D2777 outlier rejection protocol be followed. The resulting outlier free data sets can then be formatted and loaded into the AML program, which uses a spreadsheet-like format for manual data loading or can accept formatted text files directly (see AML User's Guide (29) for further details). For intralaboratory studies, the raw data from the study can be loaded into the AML program and the outlier rejection option selected. The AML program will automatically perform an outlier test on the data and compute the AML. It is not recommended that the outlier test in the AML program be used to process data from interlaboratory studies, because it will not reject labs which consistently perform poorly on the test matrices.

8.4.2.3 *Computation of the AML*

The computation approach described in this section is specifically intended for use where the true concentration of all five sample levels is known. Figure 8-4 provides an overview of how to compute an estimate of the AML from intralaboratory data; part of which requires determining the concentration of the background. Appendix B of Reference 29 provides a detailed protocol for computing an AML using intralaboratory data including determining the background concentration. When interlaboratory data are used, the grand mean of the background concentration is taken as the true concentration and the remaining test concentrations are computed by adding the spike concentrations to the background concentration.

The computation approach described in this section can be implemented with the standard deviation versus true concentration data expressed in either the exponential or the R-L form (Section 8.3). The AML program is designed to test for the best fit between the exponential and R-L model for standard deviation versus true concentration. In most cases the R-L model will provide the best fit; however, the user can visually verify the fit of either the exponential or the R-L model by selecting it from the menu. For this example, we will use the R-L equations to describe the AML computation process.

The outlier free data set is analyzed to produce expressions of the interlaboratory standard deviation versus true concentration and mean concentration versus true concentration. The interlaboratory standard deviation versus true concentration in the R-L format is:

$$s_t = \left(a_0 + a_1 T^2\right)^{1/2} \qquad \text{(eq. 114)}$$

where s_t is the interlaboratory standard deviation from the validation study and T is the true concentration of the test samples. The recovery equation is a linear regression equation in the form of:

$$X = b_0 + b_1 T \qquad \text{(eq. 115)}$$

where X is the measured concentration. Once the interlaboratory standard deviation data are expressed by equation 115 (or an exponential model), the calculation of the AML can proceed in the following manner:

1. The first step is to compute Y_{CI} which is defined as the upper 95% confidence 99% coverage tolerance limit for <u>measured concentrations</u> when the true concentration is zero:

   $$Y_{C\,I} = k s_t + b_0 \qquad \text{(eq. 116)}$$

   where k is the tolerance factor for 95% confidence, 99% coverage and the degrees of freedom, n, are equal to the number of data points at each concentration summed over all concentrations levels.

2. Substitute the interlaboratory regression equation for s_t and set T to Y_{CI} and solve for Y_{CI}:

   $$Y_{C\,I} = k\left(a_0 + a_1\left(\left(Y_{C\,I} - b_0\right)/b_1\right)^2\right)^{1/2} + b_0 \qquad \text{(eq. 117)}$$

   which requires an iterative solution. The recovery equation (eq. 116) is used to convert all computation involving the standard deviation from a mean concentration estimate (standard deviation is based on the actual data collected) to a true value.

3. Since Y_{CI} is computed from the standard deviation (a measured value), it is a measured concentration. L_{CI} is the corresponding true concentration:

$$L_{C\,I} = \left(Y_{C\,I} - b_0\right) / b_1 \qquad \text{(eq. 118)}$$

4. Once the L_{CI} is found, compute s_{CI}, the interlaboratory standard deviation at the L_{CI}, using equation (14):

$$s_{C\,I} = \left(a_0 + a_1\left(L_{C\,I}\right)^2\right)^{1/2} \qquad \text{(eq. 119)}$$

5. Compute the average instrument response (in measurement units) at 10 times the s_{CI} as:

$$Y_{Q\,I} = 10 s_{C\,I} + b_0 \qquad \text{(eq. 120)}$$

Note that b_0 is added to $10s_{CI}$ to convert Y_{QI} into a measured concentration instead of response variation.

6. Since Y_{QI} is derived from a factor times the standard deviation (a measured value) at the L_{CI}, the recovery equation (15) is used to correct Y_{QI} to the corresponding <u>true</u> concentration:

$$T_{Q\,I} = \left(Y_{Q\,I} - b_0\right) / b_1 \qquad \text{(eq. 121)}$$

7. Finally, estimate the AML by approximating the upper 95% prediction limit for a single new measurement at T_{QI}:

$$AML \approx T_{Q\,I} + \left(t s_{T_{Q\,I}} / b_1\right) \qquad \text{(eq. 122)}$$

where t is the upper 95th percentile of Student's *t*-distribution n-2-p degrees of freedom (where n is the number of data points as defined in step 1), p is the number of unknown parameters in the standard deviation model and s_{T_Q} is the interlaboratory standard deviation at T_{QI} computed by:

$$s_{T_{Q\,I}} = \left(a_0 + a_1\left(T_{Q\,I}\right)^2\right)^{1/2} \qquad \text{(eq. 123)}$$

Note equation (22) is a good approximation of the true prediction limit found in the AML program when n > 25 which is the case for interlaboratory validation studies. Figure 8-4 summarizes the AML calculation protocol.

Using the interlaboratory precision data, the equivalent of the Currie detection level, L_{DI}, can be computed. The L_{DI} will control both Type I and II errors when the true concentration is equal to L_{DI}. Operationally, the L_{DI} is computed in the following steps:

$$Y_{D\,I} = Y_{C\,I} + ks_{L_{D\,I}} \qquad \text{(eq. 124)}$$

substituting the R-L regression equation for s_{LDI} and using Y_{DI} to represent <u>mean concentrations</u>:

$$Y_{D\,I} = Y_{C\,I} + k\left(a_0 + a_1\left(\left(Y_{D\,I} - b_0\right)/b_1\right)^2\right)^{1/2} \qquad \text{(eq. 125)}$$

Y_{DI} is converted to a true concentration using the recovery equation (116):

$$L_{DI} = (Y_{DI} - b_0)/b_1 \qquad \text{(eq. 126)}$$

This definition is equivalent to the EPRI CMQL(7) developed earlier.

8.5 Determining Regulatory Compliance

The AML, as an estimate of the quantification level, L_Q, can be applied to two general regulatory cases: (1) the compliance limit is at a quantifiable level (i.e., the standard is equal to or greater than L_Q) and (2) the compliance limit is below the quantification level (e.g., some water quality-based effluent limitations).

8.5.1 *Regulatory Compliance Limit Greater Than or Equal to the Quantification Level*

If the permit regulatory compliance limit (RCL) is at a quantifiable level (i.e., RCL $\geq L_Q$), then any measurement that exceeds the RCL also exceeds L_Q. Therefore, the measurement is quantifiable and its concentration can be directly compared to the standard. A measurement above the standard indicates noncompliance.

8.5.2 *Regulatory Compliance Limit Below the Quantification Level*

In the draft guidance (1) for dealing with detection and quantification levels in the National Pollutant Discharge Elimination System (NPDES) for setting and determining compliance with water quality-based effluent limitations (WQBEL), the USEPA has proposed that when measured data are below the quantification level:

- Zero would be reported in place of all such data
- Quantification level would be computed using the interim Minimum Level (ML).

As it has been shown in the preceding sections, the ML has a number of serious deficiencies that the AML corrects. The AML is proposed as a direct replacement for the ML in permits requiring compliance with limits set below the quantification level.

8.6 ASTM Interlaboratory Detection Estimate (IDE)

EPRI has been directly involved in the development of consensus approaches to define detection and quantification in a manner that is relevant to industry's needs. As discussed in Section 8.4, EPRI played a key role with the IIAG in developing the Alternative Minimum Level which provides a scientifically based alternative to the EPA's proposed interim Minimum Level. In parallel with the AML development, EPRI participated in the American Society of Testing and Materials (ASTM) task group D19.02.04.07 and helped develop the Interlaboratory Detection Estimate (IDE) (32). The IDE addresses all of the problems with the MDL outlined in Section 8.2 and provides the utility industry with a true consensus standard for detection for use in their permits.

The IDE is defined as "the lowest concentration at which there is 90% confidence that a single measurement from a laboratory selected from the population of qualified laboratories represented in an interlaboratory study will have a true detection probability of a least 95% and a true non-detection probability of at least 99%" (32). It is an implementation of the basic principles for detection outlined by Currie (2) combined with the general approaches advocated by developers of calibration based detection levels. A measured critical level is computed from the standard deviation data and corrected to a true concentration using the recovery equation. A detection level is then computed. The key feature of the IDE is that it is based on interlaboratory standard deviation models and it uses tolerance limits to address the issue of estimating performance of multiple laboratories in the future. As an interlaboratory estimate of the detection level, the IDE can be used in compliance monitoring situations involving permit limitations expressed in terms such as “no detetectable discharge”. For a detailed presentation on the procedure by which to calculate the IDE, see reference 32: ASTM D6091 "Standard Practice for a 99%/95% Interlaboratory Detection Estimate (IDE) for Analytical Methods with Negligible Calibration Error."

The IDE and AML share a common heritage based on Currie, though they address two different issues: detection (IDE) and quantification (AML), respectively. Both use interlaboratory test data and similar models for characterizing standard deviation vs. concentration data. They both compute an L_C using a similar approach, though at slightly different tolerance limits. Together, they represent a serious effort by credible institutions to address the shortcomings in the EPA definitions for detection (MDL) and quantification (interim ML).

Building on the success of the IDE effort, ASTM is working on the development of an interlaboratory quantification estimate. EPRI will participate in that work. The AML may serve as a suitable approach for consideration by ASTM in the development of an interlaboratory quantification estimate.

8.7 Acknowledgments

Portions of this section were excerpted from Koorse (27), which was prepared collectively by Dr. Robert D. Gibbons, Professor of Biostatistics, University of Illinois; Dr. Raymond F. Maddalone, TRW; Mr. David E. Coleman, Alcoa; Dr. Babu Nott, Electric Power Research Institute; Mr. Larry LaFleur, National Council of the Paper Industry for Air and Stream Improvement, Inc.; and James K. Rice, P.E. Their work was sponsored by American Automobile Manufacturers Association, American Forest & Paper Association, Chemical Manufacturers Association, Electric Power Research Institute, National Association of Metal Finishers, American Electroplaters and Surface Finishers Society, Utility Water Act Group, and Alcoa.

8.8 References

1. USEPA, *National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-based Effluent Limitations Set Below Analytical Detection/Quantitation Levels,* March 22, 1994.
2. Currie, L.A., “Limits For Qualitative Detection And Quantitative Determination: Application To Radiochemistry,” *Analytical Chemistry,* Vol 40, p. 586 (1968).
3. Currie, L.A., “Nomenclature in Evaluation of Analytical Methods Including Detection and Quantification Capabilities,” *Pure & Appl. Chem.*, Vol. 67, No. 10, p1699 (1995).
4. Gibbons, R.D., N.E. Grams, F.H. Jarke, and K.P. Stoub. “Practical Quantitation Limits,” *Chemometrics and Intelligent Laboratory System,* Vol 12, p225 (1992).
5. USEPA, *Methods for Chemical Analysis of Water and Wastes*, USEPA-600/4-79-020, March 1979 (updated March 1983).
6. Koorse, S.J., "MCL Noncompliance: Is the Laboratory at Fault," *Journal of the AWWA,* February 1990, p53.
7. Scott, J. W., N.T. Whiddon and R. F. Maddalone, *Compliance Monitoring Detection and Quantitation Levels for Utility Aqueous Discharges*, Electric Power Research Institute, Palo Alto, CA: December 1993. Report TR- 103205.
8. Lambert, D., B. Peterson, and I. Terpenning, “Nondetects, Detection Limits And The Probability Of Detection,” *J. of the American Statistical Assoc.*, Vol. 86, p. 266 (1991).
9. Kaiser, H., "Quantitation in Elemental Analysis (Part 2)," *Anal. Chem*. Vol. 42, No. 4, p. 26A (1970).

10. Kaiser, H., *Z. Anal. Chem.*, Vol. 209, p. 1 (1965).

11. Keith, L.H., *et al.*, "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry," *Anal. Chem.*, Vol. 55, No. 14, p. 2210 (1983).

12. Glaser, J.A.; D.C. Forest, G.D. McKee, S.A. Quane, and W.L. Budde, "Trace Analysis for Wastewaters," *Environ. Sci. Technol.*, Vol. 15, No. 12, p. 1426 (1981).

13. USEPA, "Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit - Revision 1.11," *Federal Register*, *49*, (209), 43430, Friday, October 26, 1984.

14. Adams, P.B., W.O. Passmore, and D.E. Campbell, , presented at the Symposium on Trace Characterization - Chemical and Physical, National Bureau of Standards, Washington, D.C.(1966).

15. USEPA, "National Primary Drinking Water Regulations; Volatile Synthetic Organic Chemicals; proposed rule," *Federal Register, 50*, (219), 46902-46933(1985).

16. USEPA, "List (Phase 1) Of Hazardous Constituents For Ground-water Monitoring; final rule," *Federal Register*, *52,* (131), 25942-25953 (July 9, 1987).

17. Clayton, C.A., J.W. Hines, and P.D. Elkins, "Detection Limits With Specified Assurance Probabilities," *Anal. Chem.,* Vol. 59, p. 2506 (1987).

18. Kempic, J.B., "Use of Water Supply Performance Evaluation Data to Calculate Laboratory Certification Criteria and Practical Quantitation Limits for Inorganic Contaminants," presented at the 12th Annual USEPA Conference on Analysis of Pollutants in the Environment, May 10-11, 1989, Norfolk, VA.

19. USEPA, *Federal Register*, *52*, 25690 (July 8, 1987).

20. Britton, P.W., Statistician, Development and Evaluation Branch, Quality Assurance Research Division, Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, letter to Rick Brandes, Chief, Enforcement Support Branch, Office of Water Enforcement and Permits, U.S. USEPA, Washington, DC, October 22, 1990.

21. Koorse, S.J., "False Positives, Detection Limits, And Other Laboratory Imperfections: The Regulatory Implications," *Environmental Law Reporter,* Vol. 19, p. 10211 (1989).

22. Hubaux, A. and G. Vos, "Decision and Detection Limits for Linear Calibration Curves," *Anal. Chem.*, Vol. 42, No. 8, p. 849 (1970).

23. Clayton, C.A., J.W. Hines, and P.D. Elkins, "Detection Limits with Specified Assurance Probabilities," *Anal. Chem.*, Vol. 59, No. 20, p. 2506 (1987).

24. USATHAMA, PAM 11 -41, "Quality Assurance Program," January 1990.

25. Gibbons, R.D., F.H. Jarke, and K.P. Stoub, "Detection Limits for Linear Calibration Curves with Increasing Variance and Multiple Future Detection Decisions," in *Waste Testing and Quality Assurance, Vol.3*, C.E. Tatsch, editor. ASTM STP 1075, 1991, pp. 377- 390.

26. Coleman, D.E., and J.P. Auses, "Measuring Toxic Substances - A Synthesis of Method Detection Limits, Calibration, Signal-to-Noise Ratios, Significant Digits, and Practical Quantitation Limits," publicly available paper submitted for publication, 1994.

27. Koorse, S. J., “Industry Presentation for EPA’s Meeting on the Draft ‘National Guidance for the Permitting, Monitoring, and Enforcement of Water Quality-based Effluent Limitations Set Below Analytical Detection/Quantitation Levels’”, submitted to the EPA on June 21, 1995 on behalf of a coalition of American Industries by law firm of Hunton & Williams.

28. Rocke, D. M. and S. Lorenzato, “A Two-Component Model for Measurement Error in Analytical Chemistry,” *Technometrics*, Vol. 37(2), p. 176 (1995).

29. Scott, J. W., N.T. Whiddon and R. F. Maddalone, *Alternative Minimum Levels for Utility Aqueous Discharges: Chemical Analytical Measurement Guide for National Pollutant Discharge Elimination Systems (NPDES) Permits*, Electric Power Research Institute, Palo Alto, CA: November 1996. Report TR- 106220.

30. Gibbons, R.D., “A Program for Computing the Alternative Minimum Level,” Scientific Software International, Inc., Chicago, IL.

31. American Society for Testing and Materials, "Standard Practice for Determination of Precision and Bias of Applicable Methods of Committee D-19 on Water," D2777-96, *Annual Book of ASTM Standards*, 1997.

32. American Society for Testing and Materials, “Standard Practice for a 99%/95% Interlaboratory Detection Estimate (IDE) for Analytical Methods with Negligible Calibration Error,” D6091-97.

9

SUMMARY OF AMLS COMPUTED FROM THE TEST DATA

In the preceding section, the approach to computing the L_{CI}, L_{DI} and the Alternative Minimum Level (AML) was presented. Utilizing those procedures, the data from the AMQ-IV Round 2 test program were used to compute the L_{CI}, L_{DI}, AML and the RSD at the AML. The results of that analysis are shown in Table 9-1. These data are compared with the EPA-quoted detection limit for each method and the freshwater Water Quality Criteria (WQC) (1) for each element. The following sections will discuss the findings for each element separately.

Table 9-1
Summary of Alternative Minimum Levels for Arsenic, Cadmium and Chromium by GFAAS for AMQ-IV Round 2

Element	Matrix	Lower Test Conc (µg/L)	Upper Test Conc (µg/L)	L_{CI} (µg/L)	L_{DI} (µg/L)	Curve Fit RL	Curve Fit Exp	RSD[1] %	AML (µg/L)	EPA DL[2] (µg/L)	WQC[3] (µg/L)
As	RGW	4.4	98.6	2.9	5.9		X	9.3	13.7	1	190
As	GW	0.09	91.3	5.0	10.6	X		11.7	28.8	1	190
As	EST	5.4	859	18.2	39.2		X	13.4	92.9	1	190
As	AMD	8.3	942	41.6	88.9		X	13.1	213	1	190
Cd	RGW	0.01	9.5	0.25	0.51		X	9.4	1.2	0.1	1.0
Cd	GW	0.04	10.3	0.43	0.98		X	16.1	2.3	0.1	1.0
Cd	EST	0.17	97.1	2.79	7.1		X	19.8	15.8	0.1	1.0
Cd	AMD	3.5	92.8	4.1	9.2		X	15.8	21.7	0.1	1.0
Cr	RGW	0.35	91.4	2.1	4.3		X	10.5	10.4	1	10 (hex)

Table 9-1
Summary of Alternative Minimum Levels for Arsenic, Cadmium and Chromium by GFAAS for AMQ-IV Round 2

Element	Matrix	Lower Test Conc (µg/L)	Upper Test Conc (µg/L)	L_{CI} (µg/L)	L_{DI} (µg/L)	Curve Fit RL	Curve Fit Exp	RSD[1] %	AML (µg/L)	EPA DL[2] (µg/L)	WQC[3] (µg/L)
Cr	GW	0.47	100	2.6	5.4		X	11.4	13.1	1	10 (hex)
Cr	EST	2.7	955	18.7	39.4		X	11.9	93.5	1	10 (hex)
Cr	AMD	4.7	1001	15.4	34.1		X	15.0	80.8	1	10 (hex)

[1] RSD = Relative Standard Deviation at the AML

[2] Detection Limit, Methods for Chemical Analysis of Water and Wastes (EPA 600/4-79-020, Revised March 1983)

[3] Water Quality Criteria, Freshwater Criteria Continuous Concentration expressed as dissolved (60FR22236, May 4, 1995), 100 mg/L hardness where applicable

RGW = Reagent Grade Water, GW = Groundwater, EST = Estuarine, AMD = Acid Mine Drainage

9.1 Arsenic

The freshwater Criteria Continuous Concentration (CCC) water quality criteria for arsenic is 190 µg/L. The L_{DI}s (Figure 9-1) and AMLs (Figure 9-2) for arsenic were lower than the water quality criteria for all of the study matrices except the AML for acid mine drainage, which was 213 µg/L.

The L_{DI} for arsenic in reagent grade water was 5.9 µg/L compared to the EPA-quoted detection limit for the method of 1 µg/L. The L_{DI}s and AMLs were lowest for reagent grade water, followed by groundwater, estuarine and acid mine drainage, in that order.

The Relative Standard Deviations (RSDs) at the AML for arsenic were very good, ranging from 9.3 to 13.4%. As a general rule, something that is considered quantified exhibits an RSD of 10 to 20% at these concentrations.

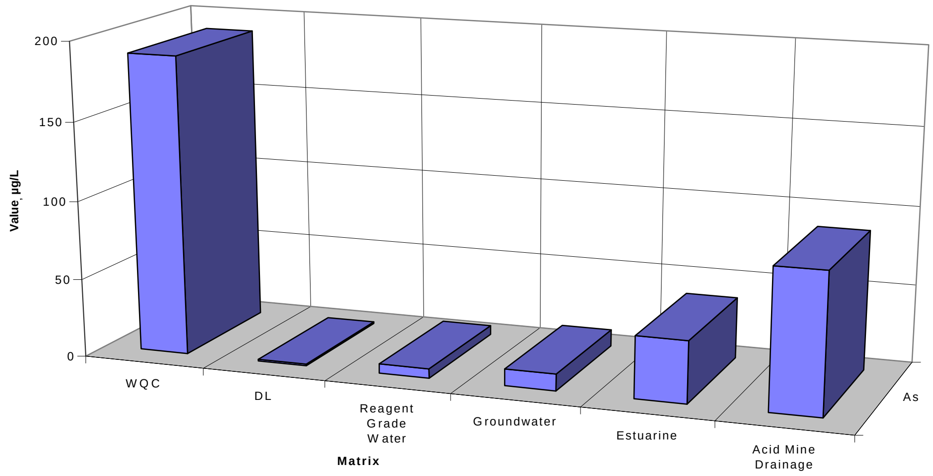


Figure 9-1 Comparison of Arsenic L_{DI}s by Matrix to WQC and DL

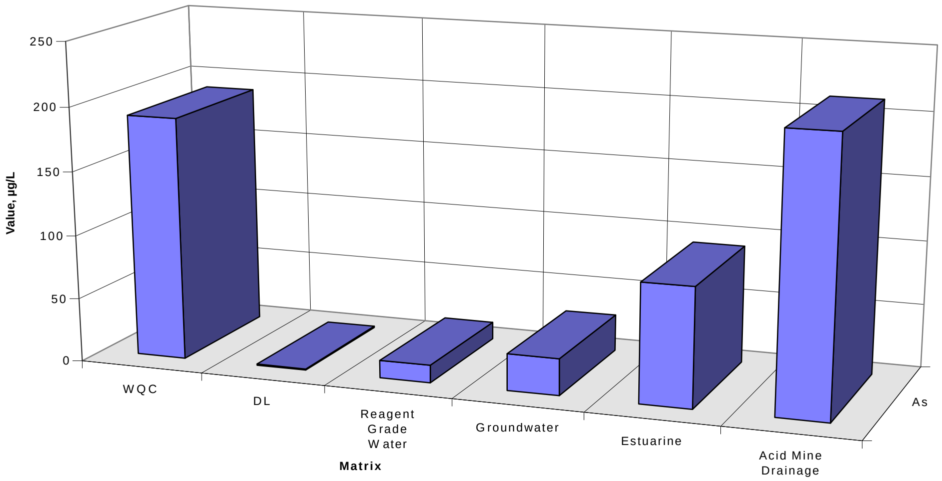


Figure 9-2 Comparison of Arsenic AMLs by Matrix to WQC and DL

9.2 Cadmium

A comparison of the cadmium L_{DI}s to the freshwater CCC water quality criteria and the detection limit quoted in the method is shown if Figure 9-3. The L_{DI}s for reagent grade water and groundwater were lower than the water quality criteria. The L_{DI}s for the more complex matrices, estuarine and acid mine drainage, were a factor of approximately 7 and 9 times higher than the water quality criteria. The L_{DI} for reagent grade water, 0.51 µg/L, was 5 times higher than the detection limit of 0.1 µg/L quoted in the EPA method.

The AMLs obtained for the cadmium data are illustrated in Figure 9-4. The cadmium AMLs ranged from 1.2 µg/L for reagent grade water to 21.7 µg/L for acid mine drainage. The AMLs obtained for all four matrices were higher than the water quality criteria of 1.0 µg/L, however the AML for reagent grade water, 1.2 µg/L was only slightly higher. The RSDs at the AML were in the 10 to 20% range.

9.3 Chromium

The L_{DI}s for chromium in reagent grade water and groundwater were lower than the water quality criteria of 10 µg/L for hexavalent chromium (Figure 9-3). The L_{DI}s for estuarine and acid mine drainage were approximately 3 times higher than the water quality criteria. The L_{DI} for reagent grade water, 4.3 µg/L, was approximately 4 times higher than the detection limit of 1 µg/L quoted in the EPA method.

The AMLs for chromium in reagent grade water and groundwater were slightly higher than the water quality criteria. The AMLs for estuarine and acid mine drainage were considerably higher. The RSDs at the AML were in the 10 to 15% range.

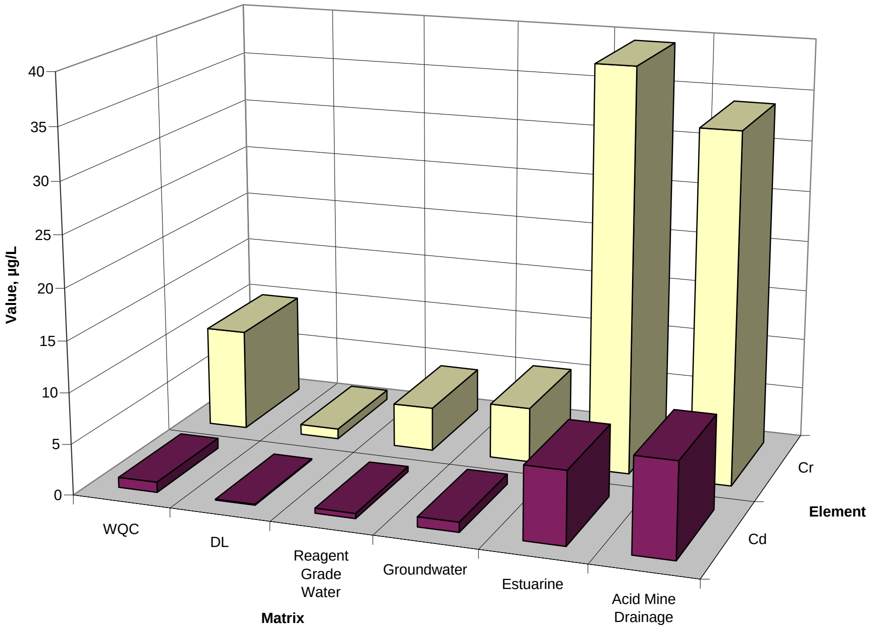


Figure 9-3 Comparison of Cadmium and Chromium L_{DI}s by Matrix to WQC and DL

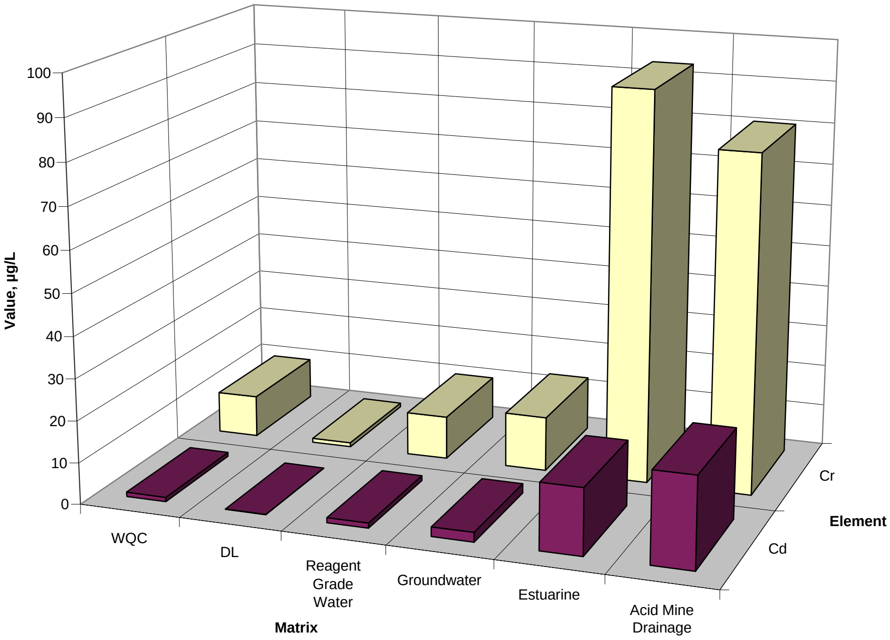


Figure 9-4 Comparison of Cadmium and Chromium AMLs by Matrix to WQC and DL

9.4 References

1. USEPA, "Stay of Federal Water Quality Criteria for Metals; Water Quality Standards; Establishment of Numeric Criteria for Priority Toxic Pollutants; States' Compliance-Revision of Metals Criteria; Final Rules," *Federal Register*, *60*, 22227-22237 (May 4, 1995).

10

CONCLUSIONS

Based on the results of the AMQ-IV validation effort, the following conclusions can be made:

- For all elements, the samples prepared by the spike and split approach taken in this project were stable over the period of time (three months) required to complete the validation effort.
- Participants were qualified to perform the analyses:
  - Over half of the GFAAS analysts had five or more years' experience, with nearly half of these having in excess of ten years' experience.
  - Seventy-two percent of the supervisors had BA/BS degrees and seventy-seven percent had more than ten years of experience.
  - Seventy-eight percent of the analysts had at least a Bachelor's degree in chemistry, biology or a related field of study.
- Ninety percent of the participants used autosamplers for sample introduction.
- Seventy-two percent of the laboratories used platform furnace instruments for all analytes, eleven percent used tube graphite furnace for all analytes, and seventeen percent used platform graphite furnace for some analytes and tube graphite furnace for others.
- All of the participants used commercially prepared standard reference materials for instrument calibration.
- Eighty percent of the data sets tested normal by the Shapiro/Wilk normality test. A normal data distribution is important since it is the basic assumption in the type of statistics that are used to reduce the data.
- Most of the data points removed were lost in the laboratory ranking step. Overall, the average outlier removal rate by laboratory ranking was 14.9%. An additional average of 2.6% of the data was removed by the individual outlier removal process.
- Recoveries of arsenic and chromium in all matrices were within ±10% for all matrices. Cadmium recoveries were within ±20% for all matrices.
- RSDs at the AML were in the 10 to 15% range for arsenic and chromium and in the 10 to 20% range for cadmium.
- Table 10-1 summarizes the performance of the methods against the detection limit quoted in the EPA method (DL) and the EPA freshwater water quality criteria

(WQC). All of the calculated L_{DI}s were higher than the corresponding detection limit published in the method. Three of the arsenic were lower than the corresponding water quality criteria.

Table 10-1
Summary of As, Cd and Cr L_{DI}s and AMLs
Compared to EPA Criteria

Element	Matrix	DL[1]	WQC[2]
Arsenic	Reagent Grade Water	H	L
Arsenic	Groundwater	H	L
Arsenic	Estuarine	H	L
Arsenic	Acid Mine Drainage	H	H
Cadmium	Reagent Grade Water	H	H
Cadmium	Groundwater	H	H
Cadmium	Estuarine	H	H
Cadmium	Acid Mine Drainage	H	H
Chromium	Reagent Grade Water	H	H
Chromium	Groundwater	H	H
Chromium	Estuarine	H	H
Chromium	Acid Mine Drainage	H	H

L = lower than criteria, H = higher than criteria

[1] L_{DI} compared to DL

[2] AML compared to WQC

A

NOMENCLATURE

Table A-1
Nomenclature Used in This Report

Abbreviation	**Description**
AAS	Atomic Absorption Spectroscopy
ACL	Acceptance Limits
ACS	American Chemical Society
Ag	Silver
AMQ	Analytical Methods Qualification
AML	Alternative Minimum Level
APO	Ash Pond Overflow
Al	Aluminum
As	Arsenic
ASTM	American Society for Testing and Materials
B	Boron
Ba	Barium
Be	Beryllium
Ca	Calcium
Cd	Cadmium
CFR	Code of Federal Regulations
CMDL	Compliance Monitoring Detection Level
CMQL	Compliance Monitoring Quantitation Level
Co	Cobalt
Cr	Chromium

Table A-1
Nomenclature Used in This Report

Abbreviation	**Description**
Cu	Copper
CVAAS	Cold Vapor AAS
DL	Detection Limit
DMR/QA	Discharge Monitoring Report/Quality Assurance
EMSL	Environmental Monitoring and Support Laboratory
EPA	Environmental Protection Agency
Fe	Iron
FLAAS	Flame AAS
FR	Federal Register
FW	Freshwater
GFAAS	Graphite Furnace AAS
GHAAS	Gaseous Hydride AAS
HCl	Hydrochloric Acid
Hg	Mercury
HNO_3	Nitric Acid
ICP-AES	Inductively Coupled Plasma - Atomic Emission Spectroscopy
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
IDL	Instrument Detection Limit
K	Potassium
L_C	Critical Level (Currie)
L_{CI}	Interlaboratory Critical Level
L_D	Detection Level (Currie)
L_{DI}	Interlaboratory Detection Level
L_Q	Determination Level (Currie)
LDRF	Laboratory Data Reporting Form
Li	Lithium

Table A-1
Nomenclature Used in This Report

Abbreviation	Description
LOD	Limit of Detection
LOQ	Limit of Quantitation
MCAW	*Methods for Chemical Analysis of Water and Wastes*, EPA 600/4-79-020 (Revised March 1983)
MCLG	Maximum Contaminant Level Goal
MDL	Method Detection Limit
Mg	Magnesium
ML	Minimum Level
Mn	Manganese
Mo	Molybdenum
MPRF	Method Parameters Reporting Form
NCWD	Non-Cooling Water Discharge
Na	Sodium
Ni	Nickel
NPDES	National Pollution Discharge Elimination System
Pb	Lead
PQL	Practical Quantitation Level
RCL	Regulatory Compliance Limit
R-L	Rocke-Lorenzato
RGW	Reagent Grade Water
RSD	Relative Standard Deviation
RW	River Water
SAUP	Sampling and Analysis of Utility Pollutants
Se	Selenium
Sn	Tin
Sr	Strontium

Table A-1
Nomenclature Used in This Report

Abbreviation	**Description**
SWD	Seawater Discharge
SWI	Seawater Intake
TCMCW	Treated Chemical Metal Cleaning Waste
TDS	Total Dissolved Solids
Ti	Titanium
Tl	Thallium
UWAG	Utility Water Act Group
V	Vanadium
WQBEL	Water Quality-Based Effluent Limitation
WQC	Water Quality Criteria
Zn	Zinc

B

LABORATORY CONTACT WORKSHEET

AMQ-TC

LABORATORY CONTACT WORKSHEET

1. Utility: ______________________________

2. Business Address ______________________________
____
____
____

3. Shipping Address ______________________________
____
____
____

4. Key Contact/Title: ______________________________

5. Telephone: ______________________________

6. Alternate Contacts:

Name	Phone Number
______________________	______________________
______________________	______________________

7. EPRI Member? Yes _____ No _____

8. Can you participate in the program? Yes ____ No ____

Comments: ____

____

9. Overload time of year? ____

10. Turnaround time? ____

11. GFAAS

Metal	Monitor?	Routine?	Monitor for Permit?	Det Lim
As				
Cd				
Cr				

12. GHAAS

As ____

13. Background Correction: ____

14. Matrices:

"Clean" Groundwater	
Acid Mine Drainage	
Estuarine Groundwater	
Reagent Grade Water	

15. Source of procedures currently used:

MCAW	________________	Standard Methods	________________
MDMES*	________________	Other	________________

* Methods for the Determination of Metals in Environmental Samples June 1991

16. Problems with / Modifications to Method __________________________

____

17. Other utilities that might want to participate?

Name	Contact

C

INSTRUCTIONS TO PARTICIPANTS

TO: AMQ-TC - PARTICIPANTS

FROM: N. T. Whiddon / J. W. Scott

SUBJECT: Instructions for AMQ-TC Test Program

With this memo we are sending you the samples to be analyzed in the Analytical Methods Qualification - Tailored Collaboration(AMQ-TC) project. Both my staff and Babu Nott, the EPRI Project Manager, greatly appreciate the cooperation you have shown in committing to complete these analyses.

PLEASE READ THE COMPLETE INSTRUCTION PACKET BEFORE BEGINNING THE ANALYSES. It is important that all participating laboratories have the same information in order for the results to be valid.

If you have any questions, don't hesitate to contact Nina Whiddon (310-813-9351) or Judy Scott (310-813-9321).

We would like all results returned by November 18, 1994 to:

Nina Whiddon
TRW
One Space Park, 01/2070
Redondo Beach, CA 90278

These results should include:

1) The completed Laboratory Data Reporting Forms for each sample. Make a copy for your records.

2) The completed Method Parameters Reporting Form.

3) The completed Laboratory Equipment and Practices Form.

We look forward to receiving your results.

TO: EPRI Analytical Method Qualification (AMQ) Participants

SUBJECT: Instructions for Determination of AMQ-TC Elements

Thank you for volunteering to participate in the AMQ-TC project.

PLEASE READ THESE INSTRUCTIONS BEFORE REMOVING SAMPLE BOTTLES FROM THE SHIPPING CARTON.

Project Goals

The goal of this project is to collect "real world" precision and bias data on analytical methods used by the utilities for utility matrices. To meet this objective, the analyses you perform for this project should be as representative of your routine analyses as possible. This means that there is no need to run practice determinations and all data should be regarded as valid. The intent is not to test your laboratory, but to develop a data base on the capabilities of the methods available for utility use. All data will be coded for reporting purposes.

This instruction packet is organized into 5 parts as follows:

Part 1. Overview of Elements and Matrices
Part 2. Sample Preparation and Analytical Procedures
Part 3. QA/QC Requirements
Part 4. Explanation of Reporting Requirements
Part 5. Explanation of Bottle Coding

Part 1. Overview of Elements and Matrices

In this round of the EPRI AMQ project you have been sent the following sets of test matrices:

- Reagent Grade Water
- Freshwater
- Estuarine Water
- Acid Mine Drainage

For each matrix, there are ten sample bottles.

A separate Laboratory Data Reporting Form is included for each sample. Please ensure that the samples you receive match those on the Reporting Forms. It is important that you note on the form the condition of each sample upon arrival. In the event that any precipitate has formed in the samples or if there is evidence of leakage, please contact TRW for discussion of whether a replacement sample is needed.

Part 2. Sample Preparation and Analytical Procedures

The procedures provided are from the EPA Methods for Chemical Analysis of Water and Wastes, (EPA-600/4-79-020, revised March 1983).

> "Metals - Atomic Absorption Methods" - general description from Methods for Chemical Analysis of Water and Wastes (MCAW)
>
> Arsenic- MCAW Method 206.2, Atomic Absorption, Furnace Technique
>
> Cadmium - MCAW Method 213.2, Atomic Absorption, Furnace Technique
>
> Chromium - MCAW Method 218.2, Atomic Absorption, Furnace Technique

For the purposes of interpretation of the round-robin test data, it is important that all procedures be followed exactly.

NOTE: CALL TRW BEFORE USING PROCEDURES OR METHODS DIFFERENT FROM THOSE SPECIFIED!

Digestion. The EPA method for arsenic includes a hydrogen peroxide digestion. TRW conducted a research study to determine if the peroxide digestion would be necessary for this study since a separate digestion for arsenic would significantly impact the workload of our volunteer laboratories. The study determined that the peroxide digestion is not necessary for the determination of arsenic in the AMQ-TC matrices. A single nitric acid digestion is sufficient for all three test elements.

The digestion procedure which will be used in this study is that designated for "total recoverable metals" in Section 4.1.4 of the MCAW general "Metals" write-up. Although this procedure calls for the addition of 5 mL/L HNO_3 at the time of sample collection/preparation, shipping restrictions made this impractical. Instead each sample was preserved by adding nitric acid to give a pH of 2 or less (maximum HNO_3 concentration approximately 0.15% by volume). Therefore, 0.5 mL of concentrated redistilled HNO_3 should be added to each 100 mL digest aliquot before heating.

NOTE: HYDROCHLORIC ACID WILL NOT BE ADDED TO DIGEST ALIQUOTS BECAUSE OF ITS INTERFERENCE WITH FURNACE ANALYSIS.

Each element being analyzed in this study requires different matrix modifiers. Please use the accompanying "Recommended AMQ-TC Sample Aliquots" flowchart as a guide in preparing your samples for analysis.

Each sample will be analyzed once beginning with the digestion step. A laboratory reagent blank should be digested and analyzed with each lot of samples prepared for analysis.

In some previous cases, a light precipitate has been reported either on arrival or after digestion. Agitate the sample bottle before taking a sample to ensure a well mixed and representative aliquot. If the amount of precipitate seems excessive, call TRW for advice. DO NOT FILTER THE SAMPLE BEFORE DIGESTION. The EPA procedure for "total recoverable metals" permits filtration of the sample after digestion to remove precipitates.

A precipitate may form during the digestion step, particularly for the high dissolved solids samples (Estuarine Water and Acid Mine Drainage). DO NOT FILTER THE DIGESTED SAMPLE BEFORE IT HAS BEEN DILUTED TO FINAL VOLUME. After the sample has been diluted to 100 mL, you may filter the sample if necessary.

Test Concentrations. For the two simplest matrices, Freshwater and Reagent Grade Water, test concentrations were selected to remain between the natural background level and the upper end of the optimum concentration range stated in the method if background concentrations permitted. Depending on the background concentrations of the elements of interest, it may be necessary to dilute some of these samples in order to remain within the linear range of the calibration curve.

The more complex matrices, Estuarine Water and Acid Mine Drainage have high total dissolved solids values which require that they be diluted for GFAAS analysis. Accordingly, these matrices have been spiked to allow a 1:10 dilution. All sample sets include at least one unspiked background sample that may have very low concentrations of the analytes of interest.

Part 3. QA/QC Instructions

Following are the QA/QC instructions for the AMQ-TC study. If your laboratory has a QA/QC program in place for GFAAS that provides equivalent quality assurance and quality control, you may use your normal procedures.

3.1 Labware

For trace elemental analysis, it is very important that all labware that comes in contact with the samples and standards be thoroughly cleaned. This includes sample containers, volumetric flasks, etc. The choice of cleaning methods is left up to the analyst as long as it can be demonstrated that the procedure does not cause any interference with the analyses.

3.2 Reagents

Acid - Due to the high sensitivity of GFAAS, only highest purity nitric acid should be used to acidify the samples and standards. Ultrex Ultrapure Reagent nitric acid has been found to be suitable.

Water - ASTM Type I water (ASTM D1193) or equivalent is required for analysis.

Standard Stock Solutions - Standard stock solutions may be prepared according to the enclosed EPA Metals Methods or purchased from a reputable commercial supplier.

3.3 Standardization

The initial standardization should consist of a solvent blank (reagent water with 0.5% redistilled nitric acid) and a minimum of three standards. The standardization should be verified by analyzing an independent quality control sample. Recovery should be +/- 10 percent of the certified value.

3.4 Standardization Checks

A standardization blank and standardization independent quality control sample should be analyzed every 10 samples. If the measured concentration exceeds +/- 10 percent of the true concentration, the analysis should be stopped and the source of error identified. All analyses since the last valid standardization check should be repeated. If the sample matrix is causing the drift, it may be necessary to perform standard additions to analyze the samples. See Section 8.5 of the EPA Metals Method (Metals for Chemical Analysis of Water and Wastes).

3.5 Spike Recovery

At least one spiked sample should be analyze with each set of samples. Spike recovery should be within +/- 10 percent.

3.6 Calculations

Be sure to include all dilution factors in your calculations!

Part 4. Explanation of Reporting Requirements

Before analyses are begun, it is important to examine the "Laboratory Data Reporting Form," "Method Parameters Reporting Form," and "Laboratory Equipment and Practices Survey," so that all information requested can be provided.

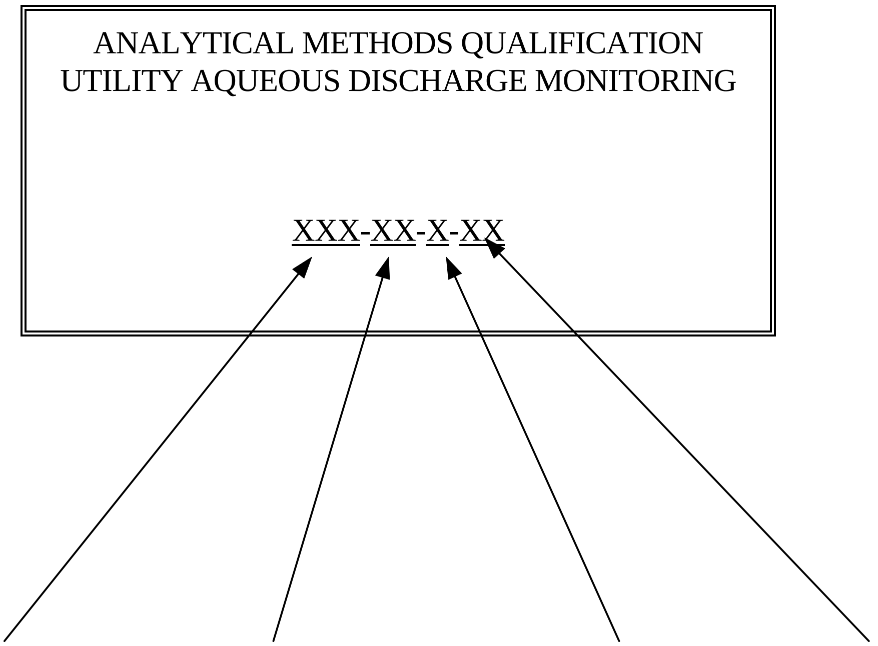
The digestion step will be performed on all test matrices, including the reagent grade water set. All samples will be analyzed only once each. This approach is required to assess the accuracy and precision of all phases of the procedure. If multiple injections or standard additions are used for a particular sample, report only a single average value for each concentration. Report both values for the matrix background sample. Where possible, please report at least three significant figures for each analytical result.

REPORT THE ACTUAL VALUE CALCULATED FOR THE SAMPLE CONCENTRATION, EVEN IF IT IS BELOW THE DETECTION LIMIT. THIS INCLUDES ZERO AND NEGATIVE VALUES.

At the conclusion of the testing, you will have an opportunity to compare your results with the averaged results of all the participating laboratories. Please retain all original data, including multiple injection or standard addition values, to facilitate follow-up review.

Part 5. Explanation of Bottle Coding

The bottle codes are designed for simple identification of sample matrix and test concentration level and to facilitate computer manipulation of test results. The several parts of the code are described in Figure 1. The first three digits comprise a code unique to your laboratory and should appear on each sample you receive. Each laboratory will be identified only by its code in the final summary of results. The two-digit Matrix Code is to facilitate your sorting of samples; matrix types and code numbers are listed on the Test Label. As a further aid to sorting the samples, the Test Labels have been color coded. All samples from a particular matrix have the same color label. The letter code is a randomly assigned code for concentration level. Youden pair studies do not permit the analyst to know the relative concentration of the test samples, so this code has meaning only for TRW. Do not try to "sort" the concentration levels alphabetically. The final two digits are for traceability of the bottle fill order.



CODE:	LABORATORY IDENTIFICATION NUMBER (THREE DIGITS)	MATRIX IDENTIFICATION (TWO DIGITS)	CONCENTRATION LEVEL (ONE LETTER)	BOTTLE CODE NUMBER (TWO DIGITS)
USE:	IDENTICAL ON ALL SAMPLES RECEIVED BY PARTICIPATING LABORATORY USED ON DATA REPORTING FORMS	PERMITS LABORATORY IDENTIFICATION OF INTERFERENCES SPECIFIC TO MATRIX	INDICATES CONCENTRATION LEVEL FOR DATA ANALYSIS (PROVIDES NO INFORMATION TO ANALYST REGARDING RELATIVE CONCENTRATION)	NUMBER USED AS IDENTIFIER OF BOTTLE FILLING ORDER

Figure 1. Sample Code System.

D

METHOD PARAMETERS REPORTING FORM

EPRI AMQ-TC
METHOD PARAMETERS REPORTING FORM

Laboratory No. _______ Laboratory Name ____

Date _________________ Analyst(s) ____

ARSENIC

Wavelength __________nm

Calibration Range _____to _____µg/L

Injection Volume _____µL

Purge Gas ____________

Purge Gas Mode: Constant Flow ___ Stop Flow ___ Pressurized ___

Type of Background Correction: Deuterium Arc __ Smith-Hieftje _ Secondary Line __

Zeeman ___ None ___ Other ______________________

		Furnace Conditions, °C, Sec							
		Drying		Ash		Atomization			
Matrix	Std Addn ?	Temp	Time	Temp	Time	Temp	Time	Pyrolytic or Non-Pyrolytic?	Tube or Platform?
RGW (05)									
FW (08)									
EST (09)									
AMD (10)									

Were other elements determined using this same furnace tube/platform?

Yes ___; List elements: ____________________

No ___

Operator experience analyzing arsenic by GFAAS:

Routine ___ Frequency ___________ Conc. levels __________ Matrices ___________

Occasional __ Frequency ___________ Conc. levels __________ Matrices ___________

None ___

How do you normally analyze arsenic? GFAAS ___ FLAAS ___ ICP-AES ___ Other ___

What is your usual digestion method for arsenic? __________________________________

Comments

____

____

EPRI AMQ-TC
METHOD PARAMETERS REPORTING FORM (Cont'd)

Laboratory No. _______ Laboratory Name ____
Date _________________ Analyst(s) ____

CADMIUM

Wavelength __________nm
Calibration Range _____to _____µg/L
Injection Volume _____µL
Purge Gas ____________
Purge Gas Mode: Constant Flow ___ Stop Flow ___ Pressurized ___
Type of Background Correction: Deuterium Arc __ Smith-Hieftje __ Secondary Line __
Zeeman ___ None ___ Other ________________________

		Furnace Conditions, °C, Sec							
		Drying		Ash		Atomization			
Matrix	Std Addn ?	Temp	Time	Temp	Time	Temp	Time	Pyrolytic or Non-Pyrolytic?	Tube or Platform?
RGW (05)									
FW (08)									
EST (09)									
AMD (10)									

Were other elements determined using this same furnace tube/platform?
Yes ___; List elements: ____________________
No ___

Operator experience analyzing cadmium by GFAAS:
Routine ___ Frequency ____________ Conc. levels __________ Matrices ____________
Occasional __ Frequency ____________ Conc. levels __________ Matrices____________
None ___

How do you normally analyze cadmium? GFAAS __ FLAAS __ ICP-AES __ Other __

What is your usual digestion method for cadmium? ________________________________

Comments
____
____

METHOD PARAMETERS REPORTING FORM (Cont'd)

Laboratory No. _______ Laboratory Name ____
Date ________________ Analyst(s) ____

CHROMIUM

Wavelength __________nm
Calibration Range _____to _____µg/L
Injection Volume _____µL
Purge Gas ____________
Purge Gas Mode: Constant Flow ___ Stop Flow ___ Pressurized ___
Type of Background Correction: Deuterium Arc __ Smith-Hieftje __ Secondary Line __
Zeeman ___ None ___ Other _______________________

		Furnace Conditions, °C, Sec							
		Drying		Ash		Atomization			
Matrix	Std Addn ?	Temp	Time	Temp	Time	Temp	Time	Pyrolytic or Non-Pyrolytic?	Tube or Platform?
RGW (05)									
FW (08)									
EST (09)									
AMD (10)									

Were other elements determined using this same furnace tube/platform?
Yes ___; List elements: ___________________
No ___

Operator experience analyzing chromium by GFAAS:
Routine ___ Frequency ___________ Conc. levels __________ Matrices ___________
Occasional __ Frequency ___________ Conc. levels __________ Matrices ___________
None ___

How do you normally analyze chromium? GFAAS __ FLAAS __ ICP-AES __ Other __

What is your usual digestion method for chromium? _____________________________

Comments
____
____

METHOD PARAMETERS REPORTING FORM (Cont'd)

Laboratory No. _______ Laboratory Name ____
Date ________________ Analyst(s) ____

<u>Miscellaneous Questions</u>

1. Aliquot introduced to furnace by:
    Glass pipet ___
    Plastic micropipet ___
    Autosampler ___
    Micro-boat ___
    Other ____________________

2. If plastic micropipet tips were used for introduction of aliquot, were they acid cleaned prior to use?
    Yes ___ Acid ______________
    No ___

3. Please identify the color and state manufacturer of the plastic micropipet tips:
    Yellow ___
    Blue ___
    Clear ___
    Manufacturer ____________________

Comments

____
____
____
____
____
____
____
____
____

E

HIGHLIGHTS OF LAB OPERATING DATA SURVEY

EPRI AMQ-TC
LABORATORY EQUIPMENT AND PRACTICES SURVEY

LABORATORY *Summary of responses for AMQ-IV Round 2 laboratories*

KEY CONTACT/PHONE ______

( ) # of laboratories responding. Total of 18 laboratories participated.

MATRICES ANALYZED (Please Circle)

(05) Reagent Grade Water
(08) Freshwater
(09) Estuarine
(10) Acid Mine Drainage

Apparatus

1. Atomic Absorption Spectrometer (AAS): *(22 instruments)*

Manufacturer	Model
Instrumentation Laboratory ______	______
Perkin-Elmer *73%*	*1100(1); 2100(2); 3030(1); 3100(1); 5000(4); 5100(7)*
Varian *18%*	*400Z(2); SpectrAA40(1); SpectrAA600Z(1)*
Jarrell-Ash *9%*	*SH-12(1); SH-4000(1)*
Other ______	______

2. Graphite Furnace manufactured by: *(22 instruments)*

Manufacturer	Model
Instrumentation Laboratory ______	______
Perkin-Elmer *73%*	*HGA400(2);HGA500(3); HGA600(2); HGA700(1); 4100(2) 5100(5)*
Varian *18%*	*400Z(2); GTA100(1); SpectrAA40(1)*
Jarrell-Ash *9%*	*188(1); SH-4000(1)*
Other ______	______

3. Type of Graphite Furnace *(17 - varied by element)*

Tube *41%*
Platform *82%*
Other ______

4. Type of AAS: *(16)*

Single Beam *31%*
Double Beam *69%*

5. AAS instrument control: *(17 - multiple responses)*

Manual______
Microprocessor __*47%*__
Outside computer __*59%*__
Other____

6. Was an autosampler used for these analyses?

Yes __*89%*__
No __*11%*__

7. If data reduction is performed by microprocessor or computer, describe program mode:

Comparison to calibration curve? (linear __*52%*__ non-linear __*24%*__)
Least squares program __*6%*__________________________
Other __*Quadratic (12%); Best-fit (6%)*__________________

8. Type of spectral emission source: (*18 - varied by element*)

Hollow cathode __*94%*__
Electrodeless discharge __*67%*__
Hollow cathode w/ changeable cathode______
Other____

9. Date of last major repair:________________

10. Date of last vendor calibration:_______________

Laboratory Standards and Sample Handling

1. Type of volumetric laboratory equipment used: *(18)* (check all that apply)

Plastic micropipets, single volume __*56%*__
Plastic micropipets, variable volume __*56%*__
Glass class A pipets __*67%*__
Plastic volumetric flasks __*11%*__
Glass volumetric flasks __*100%*__
Autodilutor __*11%*__
Other; specify_______________________________________

2. What was the source of standard reference materials used for instrument calibration and/or method of standard addition? *(18)*

Commercial *100%*
Self-prepared *6%* *(in addition to commercial)*

3. In what type of container were standards stored? *(18 labs, multiple responses)*

Glass *22%*
Polypropylene *28%*
Polyethylene *61%*
Teflon______
Other______________________________

4. What was the date of receipt or preparation of standard solutions?

Element	Date of receipt/prep	Date(s) of use

5. Which of the following were used for precleaning glassware and sample and standards storage bottles? *(18 labs - some varied cleaning for glassware, sample or standard storage)*

HCl only *11%*
HNO_3 only *39%*
Detergent only (brand) *11%*
Detergent (brand)______________, HCl and HNO_3 *11%*
Detergent (brand) ______________ and HNO_3 *33%*
Other *sample bottles purchased precleaned - 5%*
no cleaning of sample bottles - 5%

Detergents
Alconox 2
Dawn 1
Ivory 1
Liquinox 1
Micro Clean 2
Sparkleen 1
Unspecified

6. How were test samples stored? *(18)*

Refrigerated *6%*
Room temperature *94%*

Preparation and Analyses

1. Were all reagents used for sample preparation/analysis ACS reagent grade as a minimum? *(18)*

   Yes *100%*
   No______
   Specify reagent/grade________________________

2. During the digestion process, to what volume was the sample aliquot reduced? *(18)*

   2mL______ 5mL *11* 10mL *17%* 20mL *55%* 30mL *11%* 50mL____
   Other *<2 mL 6%*

3. Were precipitates present in the sample aliquot after digestion? *(17)*

   Yes *6%*; list matrices *some estuarine and AMD samples*
   No *88%*; list matrices________________________
   Don't know 6%

4. If precipitates were present, what type of filtration procedure was used to remove the precipitate? *(2)*

   Gravity______
   Vacuum *50%*
   Centrifuged______
   Settled and used supernate *50%*
   Not filtered______
   Other________________________

5. If samples were filtered, what type of filter medium was used? *(2)*

   Glass fiber______
   Cellulose paper *100%*
   Teflon______
   Membrane______
   Other________________________
   Specify brand name and porosity or filter designation number______________
   ____

6. Were other samples (i.e., standard facility samples) analyzed with subject samples.? *(18)*

Yes *17%*
No *83%*

7. Were reagent blanks carried through the sample preparation procedure? *(18)*
Yes *100%*
No______

8. Were reagents (i.e., for preservation or special instrumentation requirements) added other than those specified in the test procedure? Please include any matrix modifiers used. *(18)*

Yes *33%*
No *67%*
If yes, please specify
As $Pd + Mg(NO_3)_2$ *(1)*
Cd $PO_4 + Mg(NO_3)_2$ *(2);* $Pd + Mg(NO_3)_2$ *(1)*
Cr $Mg(NO_3)_2$ *(3);* $(NH_4)_2PO_4$ *(1)*

Palladium Chloride (1)

9. Which of the following components are used in sample chain of custody? *(18)*

Analytical request forms *67%*
Traveller sheets *28%*
Laboratory notebooks *44%*
Computer filing *61%*
Other *17%* ; Describe *Sample Prep Sheets (1); Chain of Custody (1); Archiving all raw data/documentation (1)*

10. Does your lab follow a QA/QC plan? *(17)*

Based on EPA (Section 10.2-10.3) Methods of Chemical Analysis for Water and Wastewaters *18%*
Based on EPA Handbook for Analytical QC in Water and Wastewater Laboratories *24%*
Self-generated *76%*

Based on:
EPRI QA/QC Guide (1)
Florida State EPA (1)
Wisconsin State Lab Certification (1)
Standard Methods 17th Edition (1)

Operator Experience

1. Have operators attended GFAAS training classes for the specific instrument employed? *(18)*

   Yes *61%*
   No *39%*

2. What are the number of years experience with GFAAS for the primary operator(s)?

First Operator *(18)*	Second Operator *(9)*
0 to 0.5 *6%*	0 to 0.5______
0.5 to 1 *6%*	0.5 to 1 *11%*
1 to 5 *38%*	1 to 5 *56%*
5 to 10 *28%*	5 to 10 *22%*
>10 *22%*	>10 *11%*

3. What is the degree level and major field of study of the primary operator(s)?

First Operator *(18)*

Degree	Major
No degree *11%*	
A.A. *11%*	*Chem Eng (1); Chem Tech (1)*
B.A. or B.S. *72%*	*Bio (3); Chem (6); Chem/Bio (1)Micro (1)*
M.A. or M.S.______	
Ph.D. *6%*	*Bio (1)*

Second Operator *(9)*

Degree	Major
No degree *22%*	
A.A. *11%*	*Unspecified (1)*
B.A. or B.S. *56%*	*Bio (1); Chem (1); Geo (1); Enviro* (1); *Unspecified (1)*
M.A. or M.S *11%*	*Organic Synth (1)*
Ph.D.______	

4. What is the degree level and major field of study of the laboratory supervisor responsible for AAS analysis? *(18)*

Degree	Major
No degree	
A.A.	
B.A. or B.S. *89%*	*Bio (1); Chem (10); Chem/Bio (1)* *Biochem (1); Micro (1); Enviro (1)* *Unspecified (1)*
M.A. or M.S *11%*	*Organic Synth (1); Chem (1)*
Ph.D.	

5. How many years of experience (beyond B.S.) does the above supervisor have?

0-1 6%
1-5 11%
5-10 6%
>10 77%

F

LABORATORY DATA REPORTING FORM

Laboratory Data Reporting Form

EPRI AMQ-TC – Round 1

AMQTC
Round 1
Sample ID: ________ - ________ - ________ - ____________
Matrix Type: Reagent Grade Water (05)
Freshwater (08)
Estuarine (09)
Acid Mine Drainage (10)

IMPORTANT NOTICE

Report the actual value calculated for the sample concentration, even if it is below your detection limit. Indicate your detection limit in the space provided.

PLEASE REPORT ALL RESULTS TO 0.1 ug/L.

ELEMENT	MEASURED ALIQUOT CONC (ug/L)	DILUTION FACTOR	CALCULATED CONCENTRATION OF ORIGINAL SAMPLE (ug/L)	DETECTION LIMIT * (ug/L)	ANALYST *	TESTING DATES * STARTED	TESTING DATES * COMPLETED
As							
Cd							
Cr							

Sample condition on Arrival: ____________________

Comments / Problems: ____________________

* If same for all samples in a matrix set, it is necessary to fill in only on first page of matrix set.

Please retain all data and lab records in order to answer any questions that may arise.

Make a copy of this completed form to keep with your records.

G

RAW DATA

Table G-1
Arsenic Raw Data

Lab	Matrix	As Bkg1	As Bkg2	As-1	As-2	As-3	As-4	As-5	As-6	As-7	As-8
1	5	-0.3400	0.2200	4.9400	6.8400	22.6000	31.4000	53.8000	57.2000	83.0000	84.5000
1	8	0.9700	0.9800	5.4200	8.9000	17.3000	23.0000	39.8000	49.8000	81.0000	83.0000
1	10	3.9000	5.7000	65.7000	98.2000	316.0000	387.0000	660.0000	684.0000	510.0000	670.0000
2	5	-1.5000	-2.3000	4.1000	5.4000	22.4000	28.9000	58.6000	65.4000	106.3000	124.5000
2	8	-1.2000	-0.6000	3.3000	6.2000	14.7000	18.9000	34.5000	42.2000	96.8000	109.9000
2	10	-0.5000	-1.1000	58.0000	66.0000	300.0000	37.7000	712.0000	816.0000	993.0000	1089.0000
5	5	-0.1000	-0.7000	4.3000	6.5000	20.1000	26.9000	49.3000	55.6000	89.6000	107.4000
5	8	1.0000	1.1000	5.3000	9.3000	18.9000	24.2000	41.7000	51.0000	90.9000	98.7000
5	9	14.0000	13.0000	58.0000	70.0000	254.0000	313.0000	614.0000	677.0000	907.0000	974.0000
5	10	12.0000	19.0000	82.0000	108.0000	341.0000	424.0000	731.0000	802.0000	917.0000	984.0000
6	5	-0.3000	-0.5000	3.8000	5.4000	20.6000	28.3000	56.7000	55.5000	86.4000	96.8000
6	8	-0.6000	0.2000	4.3000	9.1000	18.0000	23.5000	40.5000	49.7000	91.8000	98.2000
6	9	-4.0000	-3.0000	48.0000	48.0000	219.0000	255.0000	561.0000	611.0000	799.0000	929.0000
6	10	5.0000	5.0000	81.0000	119.0000	367.0000	481.0000	811.0000	879.0000	965.0000	1026.0000
7	5	-2.4200	-1.7200	3.1800	4.7200	23.1000	30.9000	53.8000	63.1000	90.6000	96.6000
7	8	-5.4900	-4.9500	-2.5500	3.3200	10.6000	17.8000	31.7000	39.2000	69.4000	79.0000
7	9	-2.1500	2.2600	22.2000	23.3000	163.0000	172.0000	437.0000	470.0000	641.0000	618.0000

Table G-1
Arsenic Raw Data

Lab	Matrix	As Bkg1	As Bkg2	As-1	As-2	As-3	As-4	As-5	As-6	As-7	As-8
7	10	-4.4200	5.4800	57.0000	83.0000	321.0000	403.0000	697.0000	772.0000	841.0000	938.0000
8	5	1.2000	0.6000	4.2000	6.7000	17.8000	25.8000	10.8000	47.8000	89.4000	89.4000
8	8	2.4000	0.0000	5.2000	9.2000	15.9000	21.7000	33.7000	38.5000	75.3000	67.5000
8	9	3.0000	0.2000	48.4000	65.7000	238.0000	318.0000	422.0000	384.0000	864.0000	760.0000
8	10	0.0000	0.0000	18.3000	20.7000	45.4000	40.8000	836.0000	944.0000	928.0000	992.0000
10	5	-0.8000	1.3000	1.8000	7.3000	22.5000	29.4000	57.5000	66.0000	93.8000	89.9000
10	8	-1.7000	-2.3000	-1.3000	-1.4000	25.5000	26.2000	51.3000	58.1000	68.9000	90.2000
10	9	5.7000	19.5000	36.0000	1.0000	228.0000	213.0000	487.0000	727.0000	727.0000	1040.0000
10	10	36.0000	6.0000	45.0000	58.0000	217.0000	474.0000	739.0000	668.0000	790.0000	917.0000
11	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
11	8	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
11	10	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
15	5	1.1000	0.4000	5.4000	7.0000	19.0000	25.6000	46.0000	53.1000	93.6000	99.3000
15	8	0.0000	0.6000	4.6000	8.5000	16.7000	22.1000	41.1000	51.5000	92.6000	7.9000
15	9	4.2000	2.7000	32.0000	42.0000	185.0000	242.0000	494.0000	568.0000	749.0000	820.0000
15	10	4.7000	3.0000	62.0000	81.0000	288.0000	348.0000	736.0000	595.0000	775.0000	931.0000
16	5	9.4000	5.5000	8.3000	10.0000	31.1000	36.1000	62.2000	73.3000	90.0000	107.0000
16	8	12.2000	7.2000	13.3000	18.3000	28.9000	42.8000	59.4000	64.4000	95.6000	101.0000
16	9	60.0000	60.0000	167.0000	66.0000	367.0000	254.0000	722.0000	833.0000	723.0000	888.0000
16	10	52.2000	9.0000	175.0000	122.0000	422.0000	589.0000	800.0000	770.0000	988.0000	112.0000
17	5	0.0000	0.0000	6.0000	8.0000	24.0000	32.0000	62.0000	68.0000	127.2000	129.0000
17	8	1.0000	2.0000	6.0000	10.0000	27.0000	27.0000	48.0000	56.0000	116.0000	120.0000

Table G-1
Arsenic Raw Data

Lab	Matrix	As Bkg1	As Bkg2	As-1	As-2	As-3	As-4	As-5	As-6	As-7	As-8
17	9	3.0000	3.0000	48.0000	58.0000	261.0000	280.0000	560.0000	620.0000	840.0000	880.0000
17	10	6.0000	57.0000	100.0000	140.0000	400.0000	490.0000	220.0000	930.0000	1080.0000	770.0000
20	5	0.5000	2.4000	6.1000	7.5000	24.2000	29.8000	52.9000	58.4000	87.5000	103.1000
20	8	0.6000	1.5000	5.7000	11.0000	21.0000	26.3000	44.1000	95.5000	94.0000	101.5000
20	9	26.0000	20.0000	67.0000	67.0000	275.0000	320.0000	664.0000	657.0000	896.0000	969.0000
20	10	13.0000	18.0000	94.0000	118.0000	364.0000	448.0000	779.0000	855.0000	952.0000	1062.0000
21	5	-1.0000	-1.0000	4.4000	6.4000	22.2000	28.3000	50.0000	57.0000	87.4000	99.6000
21	8	0.8000	0.6000	5.0000	8.4000	17.3000	22.5000	37.8000	44.5000	79.3000	79.6000
21	9	3.0000	2.7000	44.5000	55.0000	220.0000	269.0000	532.0000	578.0000	791.0000	835.0000
21	10	37.0000	37.9000	59.0000	87.0000	310.0000	389.0000	633.0000	675.0000	765.0000	819.0000
22	5	11.0000	10.5600	11.3000	11.6000	27.1000	34.1000	55.5000	64.6000	96.2000	120.8000
22	8	12.7000	12.7000	13.0000	14.4000	20.1000	24.6000	35.9000	42.2000	66.7000	71.6000
22	9	14.0000	16.5000	51.9000	66.2000	269.0000	311.0000	491.0000	562.0000	848.0000	793.0000
24	5	0.0000	1.0800	3.8100	7.4200	22.0000	29.4000	56.2000	67.9000	87.0000	126.0000
24	8	1.4900	0.0000	7.2200	8.3200	18.6000	18.5000	42.0000	40.1000	90.5000	96.9000
24	9	6.0000	6.2000	47.1000	55.0000	152.0000	168.0000	318.0000	718.0000	919.0000	1167.0000
24	10	21.4000	21.5000	96.6000	158.0000	375.0000	680.0000	779.0000	950.0000	1090.0000	1156.0000
25	5	0.0000	0.0000	5.7000	6.9000	22.6000	27.6000	43.2000	58.4000	89.2000	107.0000
25	8	0.0000	0.0000	6.2000	9.3000	13.7000	22.6000	45.1000	44.8000	80.0000	85.6000
25	9	3.2000	3.2000	42.9000	56.1000	240.0000	267.0000	594.0000	535.0000	861.0000	939.0000
25	10	0.0000	0.0000	52.8000	294.0000	380.0000	384.0000	648.0000	713.0000	818.0000	889.0000
26	5	-0.5000	-0.8000	5.2000	6.7000	22.0000	28.5000	50.8000	59.3000	88.7000	99.5000

Table G-1
Arsenic Raw Data

Lab	Matrix	As Bkg1	As Bkg2	As-1	As-2	As-3	As-4	As-5	As-6	As-7	As-8
26	8	0.2000	0.3000	4.5000	10.0000	19.2000	24.6000	40.6000	51.7000	90.3000	94.9000
26	9	-6.0000	10.0000	54.0000	55.0000	251.0000	313.0000	603.0000	677.0000	831.0000	924.0000
26	10	-1.0000	0.0000	64.0000	84.0000	323.0000	394.0000	725.0000	737.0000	904.0000	973.0000
27	5	-1.0000	0.0000	4.0000	7.0000	19.0000	25.0000	47.0000	54.0000	88.0000	88.0000
27	8	-2.0000	-2.0000	2.0000	6.0000	14.0000	20.0000	36.0000	45.0000	81.0000	97.0000
27	9	-20.0000	-30.0000	20.0000	30.0000	190.0000	240.0000	530.0000	530.0000	770.0000	770.0000
27	10	-20.0000	-10.0000	60.0000	90.0000	350.0000	430.0000	670.0000	810.0000	840.0000	960.0000

Table G-2
Cadmium Raw Data

Lab	Matrix	Cd Bkg1	Cd Bkg2	Cd-1	Cd-2	Cd-3	Cd-4	Cd-5	Cd-6	Cd-7	Cd-8
1	5	0.0000	-0.0200	6.1100	8.5100	15.3000	21.1000	49.9000	56.9000	84.8000	101.8000
1	8	0.0900	0.1300	8.4800	6.0500	14.8000	21.6000	42.5000	45.9000	83.5000	92.2000
1	10	12.4000	11.4000	40.5000	58.1000	165.1000	214.7000	399.0000	440.0000	1123.0000	1022.0000
2	5	-0.2000	-0.3000	5.1000	8.4000	15.4000	21.3000	38.3000	42.4000	65.6000	80.6000
2	8	-0.1000	-0.5000	4.4000	7.5000	17.6000	21.5000	45.1000	48.0000	97.0000	106.0000
2	10	2.0000	3.0000	47.0000	66.0000	210.0000	279.0000	430.0000	410.0000	744.0000	732.0000
5	5	0.5000	0.2000	5.3000	8.7000	15.2000	21.5000	47.1000	55.2000	85.3000	101.3000
5	8	0.6000	0.5000	4.7000	7.4000	19.5000	22.7000	50.3000	58.9000	80.9000	93.3000
5	9	2.0000	0.0000	55.0000	74.0000	283.0000	372.0000	618.0000	697.0000	820.0000	932.0000
5	10	3.0000	3.0000	41.0000	59.0000	180.0000	247.0000	378.0000	436.0000	752.0000	817.0000
6	5	-0.7000	-0.9000	4.3000	7.6000	15.4000	22.0000	49.2000	55.0000	85.9000	96.3000
6	8	-0.1000	1.6000	3.3000	6.4000	15.4000	19.1000	44.3000	49.6000	75.9000	90.7000
6	9	-7.0000	-10.0000	48.0000	70.0000	282.0000	337.0000	648.0000	732.0000	816.0000	944.0000
6	10	0.0000	-7.0000	39.0000	54.0000	206.0000	290.0000	446.0000	505.0000	863.0000	951.0000
7	5	-0.4930	-0.6500	6.0800	8.1400	16.1000	23.2000	49.8000	56.1000	81.9000	92.6000
7	8	0.1410	-0.4470	4.4700	8.7400	20.4000	26.8000	55.4000	64.8000	86.2000	110.0000
7	9	1.5500	1.7300	45.5000	60.0000	323.0000	407.0000	645.0000	720.0000	797.0000	895.0000
7	10	5.1200	4.8200	43.4000	62.0000	206.0000	275.0000	418.0000	468.0000	796.0000	822.0000
8	5	2.5000	-1.2000	5.0000	10.1000	13.3000	22.0000	50.2000	46.1000	84.1000	89.9000
8	8	0.0000	1.4000	5.4000	9.4000	23.4000	23.1000	57.6000	56.9000	103.0000	109.0000
8	9	2.8000	0.9000	55.3000	75.5000	269.0000	286.0000	534.0000	601.0000	726.0000	818.0000

Table G-2
Cadmium Raw Data

Lab	Matrix	Cd Bkg1	Cd Bkg2	Cd-1	Cd-2	Cd-3	Cd-4	Cd-5	Cd-6	Cd-7	Cd-8
8	10	0.9000	0.4000	30.3000	52.2000	172.0000	257.0000	394.0000	479.0000	794.0000	930.0000
10	5	0.7000	0.8000	6.1000	7.5000	15.7000	22.3000	45.1000	57.1000	82.7000	87.0000
10	8	0.8000	1.0000	3.9000	6.1000	15.9000	21.3000	53.1000	59.1000	78.5000	84.9000
10	9	29.5000	4.0000	58.5000	90.5000	372.5000	430.5000	729.5000	764.5000	980.0000	1050.0000
10	10	42.5000	100.0000	100.5000	73.5000	308.0000	343.0000	463.0000	466.0000	971.0000	1072.5000
11	5	-0.1000	-0.1000	5.6000	8.1000	15.8000	21.9000	47.2000	53.7000	84.7000	88.2000
11	8	0.2000	-0.1000	4.9000	8.3000	20.0000	25.1000	54.7000	64.3000	86.1000	104.0000
11	10	7.1000	8.2000	51.7000	69.8000	215.0000	276.0000	451.0000	505.0000	902.0000	990.0000
15	5	0.6000	1.1000	5.9000	8.5000	16.2000	22.0000	49.9000	51.6000	82.7000	80.6000
15	8	1.1000	0.9000	4.4000	7.5000	18.1000	23.3000	48.2000	54.1000	92.3000	98.9000
15	9	1.1000	1.0000	47.0000	67.0000	261.0000	333.0000	532.0000	642.0000	728.0000	878.0000
15	10	3.9000	4.1000	40.0000	59.0000	192.0000	247.0000	396.0000	413.0000	718.0000	855.0000
16	5	2.2000	7.8000	10.6000	11.1000	22.8000	28.3000	36.7000	67.8000	67.8000	88.3000
16	8	7.2000	6.1000	11.1000	16.7000	32.8000	38.9000	75.6000	90.0000	125.6000	143.9000
16	9	8.0000	84.0000	60.0000	100.0000	378.0000	269.0000	471.0000	582.0000	644.0000	700.0000
16	10	22.2000	8.9000	54.4000	111.0000	233.0000	322.0000	478.0000	460.0000	830.0000	910.0000
17	5	1.0000	0.0000	6.0000	9.0000	16.0000	23.0000	52.0000	59.0000	89.0000	119.7000
17	8	6.0000	5.0000	5.0000	9.0000	28.0000	28.0000	75.0000	70.0000	100.0000	30.0000
17	9	6.0000	3.0000	66.0000	94.0000	376.0000	420.0000	690.0000	780.0000	910.0000	1249.0000
17	10	6.0000	4.0000	53.0000	69.0000	223.0000	303.0000	512.0000	580.0000	1020.0000	1211.0000
20	5	1.5000	0.7000	5.1000	7.2000	16.8000	22.7000	45.0000	52.6000	81.2000	90.4000
20	8	1.0000	0.6000	266.0000	10.1000	20.5000	25.7000	54.1000	67.6000	90.7000	96.4000

Table G-2
Cadmium Raw Data

Lab	Matrix	Cd Bkg1	Cd Bkg2	Cd-1	Cd-2	Cd-3	Cd-4	Cd-5	Cd-6	Cd-7	Cd-8
20	9	27.0000	23.0000	80.0000	90.0000	329.0000	390.0000	682.0000	735.0000	873.0000	972.0000
20	10	24.0000	18.0000	87.0000	96.0000	266.0000	343.0000	507.0000	563.0000	937.0000	1052.0000
21	5	4.8000	0.1000	6.8000	10.0000	17.4000	22.9000	48.7000	54.1000	80.0000	95.7000
21	8	4.1000	2.1000	7.1000	8.6000	18.7000	25.6000	50.6000	59.7000	82.2000	97.4000
21	9	1.0000	0.5000	61.0000	76.0000	293.0000	378.0000	596.0000	698.0000	823.0000	905.0000
21	10	2.9000	2.0000	36.0000	53.0000	171.0000	244.0000	376.0000	439.0000	765.0000	869.0000
22	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
22	8	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
22	9	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
24	5	0.0000	0.9800	5.5000	11.1000	19.8000	29.2000	70.5000	66.3000	62.8000	97.6000
24	8	0.2700	0.0000	4.0100	11.7000	29.1000	31.3000	54.5000	83.8000	87.2000	87.6000
24	9	7.0000	0.0000	74.2000	67.1000	397.0000	487.0000	717.0000	548.0000	734.0000	801.0000
24	10	5.2000	0.0000	32.9000	73.4000	230.0000	258.0000	487.0000	496.0000	450.0000	106.0000
25	5	0.3000	0.0000	7.1000	8.4000	18.6000	18.4000	41.6000	57.6000	88.0000	92.4000
25	8	0.4000	0.0000	5.0000	8.9000	21.8000	16.8000	49.6000	51.7000	77.7000	101.2000
25	9	2.4000	0.0000	62.7000	81.4000	321.0000	409.0000	667.0000	768.0000	848.0000	949.0000
25	10	0.0000	2.4000	58.3000	81.4000	269.0000	295.0000	459.0000	529.0000	1020.0000	949.0000
26	5	0.2000	0.2000	5.8000	8.1000	15.8000	21.8000	49.2000	56.0000	86.0000	99.0000
26	8	0.0000	-0.1000	5.0000	7.7000	19.3000	23.8000	53.0000	73.5000	92.0000	103.0000
26	9	3.0000	0.0000	60.0000	73.0000	284.0000	335.0000	625.0000	670.0000	800.0000	950.0000
26	10	4.0000	4.0000	53.0000	81.0000	206.0000	268.0000	460.0000	490.0000	890.0000	950.0000
27	5	0.0000	1.0000	6.0000	10.0000	15.0000	16.0000	43.0000	45.0000	88.0000	78.0000

Table G-2
Cadmium Raw Data

Lab	Matrix	Cd Bkg1	Cd Bkg2	Cd-1	Cd-2	Cd-3	Cd-4	Cd-5	Cd-6	Cd-7	Cd-8
27	8	-1.0000	0.0000	6.0000	9.0000	20.0000	24.0000	48.0000	64.0000	86.0000	99.0000
27	9	10.0000	10.0000	70.0000	80.0000	280.0000	390.0000	550.0000	600.0000	790.0000	810.0000
27	10	10.0000	20.0000	40.0000	80.0000	170.0000	220.0000	300.0000	460.0000	780.0000	870.0000

Table G-3
Chromium Raw Data

Lab	Matrix	Cr Bkg1	Cr Bkg2	Cr-1	Cr-2	Cr-3	Cr-4	Cr-5	Cr-6	Cr-7	Cr-8
1	5	0.0000	-0.0200	6.1100	8.5100	15.3000	21.1000	49.9000	56.9000	84.8000	101.8000
1	8	0.0900	0.1300	8.4800	6.0500	14.8000	21.6000	42.5000	45.9000	83.5000	92.2000
1	10	12.4000	11.4000	40.5000	58.1000	165.1000	214.7000	399.0000	440.0000	1123.0000	1022.0000
2	5	-0.2000	-0.3000	5.1000	8.4000	15.4000	21.3000	38.3000	42.4000	65.6000	80.6000
2	8	-0.1000	-0.5000	4.4000	7.5000	17.6000	21.5000	45.1000	48.0000	97.0000	106.0000
2	10	2.0000	3.0000	47.0000	66.0000	210.0000	279.0000	430.0000	410.0000	744.0000	732.0000
5	5	0.5000	0.2000	5.3000	8.7000	15.2000	21.5000	47.1000	55.2000	85.3000	101.3000
5	8	0.6000	0.5000	4.7000	7.4000	19.5000	22.7000	50.3000	58.9000	80.9000	93.3000
5	9	2.0000	0.0000	55.0000	74.0000	283.0000	372.0000	618.0000	697.0000	820.0000	932.0000
5	10	3.0000	3.0000	41.0000	59.0000	180.0000	247.0000	378.0000	436.0000	752.0000	817.0000
6	5	-0.7000	-0.9000	4.3000	7.6000	15.4000	22.0000	49.2000	55.0000	85.9000	96.3000
6	8	-0.1000	1.6000	3.3000	6.4000	15.4000	19.1000	44.3000	49.6000	75.9000	90.7000
6	9	-7.0000	-10.0000	48.0000	70.0000	282.0000	337.0000	648.0000	732.0000	816.0000	944.0000
6	10	0.0000	-7.0000	39.0000	54.0000	206.0000	290.0000	446.0000	505.0000	863.0000	951.0000
7	5	-0.4930	-0.6500	6.0800	8.1400	16.1000	23.2000	49.8000	56.1000	81.9000	92.6000
7	8	0.1410	-0.4470	4.4700	8.7400	20.4000	26.8000	55.4000	64.8000	86.2000	110.0000
7	9	1.5500	1.7300	45.5000	60.0000	323.0000	407.0000	645.0000	720.0000	797.0000	895.0000
7	10	5.1200	4.8200	43.4000	62.0000	206.0000	275.0000	418.0000	468.0000	796.0000	822.0000
8	5	2.5000	-1.2000	5.0000	10.1000	13.3000	22.0000	50.2000	46.1000	84.1000	89.9000
8	8	0.0000	1.4000	5.4000	9.4000	23.4000	23.1000	57.6000	56.9000	103.0000	109.0000
8	9	2.8000	0.9000	55.3000	75.5000	269.0000	286.0000	534.0000	601.0000	726.0000	818.0000

Table G-3
Chromium Raw Data

Lab	Matrix	Cr Bkg1	Cr Bkg2	Cr-1	Cr-2	Cr-3	Cr-4	Cr-5	Cr-6	Cr-7	Cr-8
8	10	0.9000	0.4000	30.3000	52.2000	172.0000	257.0000	394.0000	479.0000	794.0000	930.0000
10	5	0.7000	0.8000	6.1000	7.5000	15.7000	22.3000	45.1000	57.1000	82.7000	87.0000
10	8	0.8000	1.0000	3.9000	6.1000	15.9000	21.3000	53.1000	59.1000	78.5000	84.9000
10	9	29.5000	4.0000	58.5000	90.5000	372.5000	430.5000	729.5000	764.5000	980.0000	1050.0000
10	10	42.5000	100.0000	100.5000	73.5000	308.0000	343.0000	463.0000	466.0000	971.0000	1072.5000
11	5	-0.1000	-0.1000	5.6000	8.1000	15.8000	21.9000	47.2000	53.7000	84.7000	88.2000
11	8	0.2000	-0.1000	4.9000	8.3000	20.0000	25.1000	54.7000	64.3000	86.1000	104.0000
11	10	7.1000	8.2000	51.7000	69.8000	215.0000	276.0000	451.0000	505.0000	902.0000	990.0000
15	5	0.6000	1.1000	5.9000	8.5000	16.2000	22.0000	49.9000	51.6000	82.7000	80.6000
15	8	1.1000	0.9000	4.4000	7.5000	18.1000	23.3000	48.2000	54.1000	92.3000	98.9000
15	9	1.1000	1.0000	47.0000	67.0000	261.0000	333.0000	532.0000	642.0000	728.0000	878.0000
15	10	3.9000	4.1000	40.0000	59.0000	192.0000	247.0000	396.0000	413.0000	718.0000	855.0000
16	5	2.2000	7.8000	10.6000	11.1000	22.8000	28.3000	36.7000	67.8000	67.8000	88.3000
16	8	7.2000	6.1000	11.1000	16.7000	32.8000	38.9000	75.6000	90.0000	125.6000	143.9000
16	9	8.0000	84.0000	60.0000	100.0000	378.0000	269.0000	471.0000	582.0000	644.0000	700.0000
16	10	22.2000	8.9000	54.4000	111.0000	233.0000	322.0000	478.0000	460.0000	830.0000	910.0000
17	5	1.0000	0.0000	6.0000	9.0000	16.0000	23.0000	52.0000	59.0000	89.0000	119.7000
17	8	6.0000	5.0000	5.0000	9.0000	28.0000	28.0000	75.0000	70.0000	100.0000	30.0000
17	9	6.0000	3.0000	66.0000	94.0000	376.0000	420.0000	690.0000	780.0000	910.0000	1249.0000
17	10	6.0000	4.0000	53.0000	69.0000	223.0000	303.0000	512.0000	580.0000	1020.0000	1211.0000
20	5	1.5000	0.7000	5.1000	7.2000	16.8000	22.7000	45.0000	52.6000	81.2000	90.4000
20	8	1.0000	0.6000	266.0000	10.1000	20.5000	25.7000	54.1000	67.6000	90.7000	96.4000

Table G-3
Chromium Raw Data

Lab	Matrix	Cr Bkg1	Cr Bkg2	Cr-1	Cr-2	Cr-3	Cr-4	Cr-5	Cr-6	Cr-7	Cr-8
20	9	27.0000	23.0000	80.0000	90.0000	329.0000	390.0000	682.0000	735.0000	873.0000	972.0000
20	10	24.0000	18.0000	87.0000	96.0000	266.0000	343.0000	507.0000	563.0000	937.0000	1052.0000
21	5	4.8000	0.1000	6.8000	10.0000	17.4000	22.9000	48.7000	54.1000	80.0000	95.7000
21	8	4.1000	2.1000	7.1000	8.6000	18.7000	25.6000	50.6000	59.7000	82.2000	97.4000
21	9	1.0000	0.5000	61.0000	76.0000	293.0000	378.0000	596.0000	698.0000	823.0000	905.0000
21	10	2.9000	2.0000	36.0000	53.0000	171.0000	244.0000	376.0000	439.0000	765.0000	869.0000
22	5	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
22	8	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
22	9	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
24	5	0.0000	0.9800	5.5000	11.1000	19.8000	29.2000	70.5000	66.3000	62.8000	97.6000
24	8	0.2700	0.0000	4.0100	11.7000	29.1000	31.3000	54.5000	83.8000	87.2000	87.6000
24	9	7.0000	0.0000	74.2000	67.1000	397.0000	487.0000	717.0000	548.0000	734.0000	801.0000
24	10	5.2000	0.0000	32.9000	73.4000	230.0000	258.0000	487.0000	496.0000	450.0000	106.0000
25	5	0.3000	0.0000	7.1000	8.4000	18.6000	18.4000	41.6000	57.6000	88.0000	92.4000
25	8	0.4000	0.0000	5.0000	8.9000	21.8000	16.8000	49.6000	51.7000	77.7000	101.2000
25	9	2.4000	0.0000	62.7000	81.4000	321.0000	409.0000	667.0000	768.0000	848.0000	949.0000
25	10	0.0000	2.4000	58.3000	81.4000	269.0000	295.0000	459.0000	529.0000	1020.0000	949.0000
26	5	0.2000	0.2000	5.8000	8.1000	15.8000	21.8000	49.2000	56.0000	86.0000	99.0000
26	8	0.0000	-0.1000	5.0000	7.7000	19.3000	23.8000	53.0000	73.5000	92.0000	103.0000
26	9	3.0000	0.0000	60.0000	73.0000	284.0000	335.0000	625.0000	670.0000	800.0000	950.0000
26	10	4.0000	4.0000	53.0000	81.0000	206.0000	268.0000	460.0000	490.0000	890.0000	950.0000
27	5	0.0000	1.0000	6.0000	10.0000	15.0000	16.0000	43.0000	45.0000	88.0000	78.0000

Table G-3
Chromium Raw Data

Lab	Matrix	Cr Bkg1	Cr Bkg2	Cr-1	Cr-2	Cr-3	Cr-4	Cr-5	Cr-6	Cr-7	Cr-8
27	8	-1.0000	0.0000	6.0000	9.0000	20.0000	24.0000	48.0000	64.0000	86.0000	99.0000
27	9	10.0000	10.0000	70.0000	80.0000	280.0000	390.0000	550.0000	600.0000	790.0000	810.0000
27	10	10.0000	20.0000	40.0000	80.0000	170.0000	220.0000	300.0000	460.0000	780.0000	870.0000

H

STATCALC INPUT/OUTPUT

For each element, sorted by matrix, the following tables are presented:

- Data File (.DAT) - Displays original raw data submitted by each laboratory.
- Data Validation File (.DA~) - Audit record documenting the fate of each original data point. Includes information on values removed by lab ranking and outlier testing.
- Final Data File (.DAF) - Final data set submitted for statistical processing after removal of outliers.
- Data Preparation File (.PRP) - Displays the results of the factor of 5 screening, laboratory ranking, individual outlier removal, and normality testing.
- Summary Statistics (.STT) - Contains recovery, single operator standard deviation, and overall standard deviation results at each concentration; results of bias testing; linear and curvilinear equations for single operator and overall standard deviation; linear regression equations for recovery; and linear regression equations for both single operator and overall standard deviation versus recovery (obtained by substitution).

The Data Validation and Final Data files have a flag field to the left of each value which is used to provide information about the value. The following table lists the flags and their meanings.

Flag	Description	File
r	Value removed by lab ranking test	.DA~, .DAF
o	Value removed by individual outlier removal test	.DA~, .DAF
!	Value flagged for removal by lab ranking test but retained. Removal would have exceeded 20% cap on data removal by lab ranking.	.DA~
?	Value flagged for removal by individual outlier test but retained. Removal would have exceeded 10% cap on data removed by outlier testing.	.DA~
e	Temporary fill value for missing value. Calculated by linear regression through remaining data submitted by laboratory. Used for lab ranking test and then deleted.	.DA~
*	No value submitted	.DAF

```
as-5.dat

As     5   1     4.9400    6.8400   22.6000   31.4000   53.8000   57.2000   83.0000   84.5000
As     5   2     4.1000    5.4000   22.4000   28.9000   58.6000   65.4000  106.3000  124.5000
As     5   5     4.3000    6.5000   20.1000   26.9000   49.3000   55.6000   89.6000  107.4000
As     5   6     3.8000    5.4000   20.6000   28.3000   56.7000   55.5000   86.4000   96.8000
As     5   7     3.1800    4.7200   23.1000   30.9000   53.8000   63.1000   90.6000   96.6000
As     5   8     4.2000    6.7000   17.8000   25.8000   10.8000   47.8000   89.4000   89.4000
As     5  10     1.8000    7.3000   22.5000   29.4000   57.5000   66.0000   93.8000   89.9000
As     5  15     5.4000    7.0000   19.0000   25.6000   46.0000   53.1000   93.6000   99.3000
As     5  16     8.3000   10.0000   31.1000   36.1000   62.2000   73.3000   90.0000  107.0000
As     5  17     6.0000    8.0000   24.0000   32.0000   62.0000   68.0000  127.2000  129.0000
As     5  20     6.1000    7.5000   24.2000   29.8000   52.9000   58.4000   87.5000  103.1000
As     5  21     4.4000    6.4000   22.2000   28.3000   50.0000   57.0000   87.4000   99.6000
As     5  22    11.3000   11.6000   27.1000   34.1000   55.5000   64.6000   96.2000  120.8000
As     5  24     3.8100    7.4200   22.0000   29.4000   56.2000   67.9000   87.0000  126.0000
As     5  25     5.7000    6.9000   22.6000   27.6000   43.2000   58.4000   89.2000  107.0000
As     5  26     5.2000    6.7000   22.0000   28.5000   50.8000   59.3000   88.7000   99.5000
As     5  27     4.0000    7.0000   19.0000   25.0000   47.0000   54.0000   88.0000   88.0000
```

```
File Name:  as-5
Data Validation File (.DA~)

******************************************************************************
***                   Parameter and Data Validation File                   ***
******************************************************************************
   Analyte:  As             Matrix:  Reagent Grade Water
   Project:  AMQ-TC      Matrix ID:   5
      Date:  12/13/1995     Method:  GFAAS
     Pairs:  4
     Units:  ug/L

---------------------------------------------------------------------------------------------------------
Level          1          2            3          4            5          6            7          8
---------------------------------------------------------------------------------------------------------
Spike         4.3521     2.0000      14.8000     6.4000      21.7000     8.1000      30.0000    11.3000
Spike
Increment      .0000     2.0000      16.8000    23.2000      44.9000    53.0000      83.0000    94.3000
---------------------------------------------------------------------------------------------------------

                 Final Concentration
         ------------------------------------------------------------------------------------------------
Lab ID        4.3521     6.3521      21.1521    27.5521      49.2521    57.3521      87.3521    98.6521
---------------------------------------------------------------------------------------------------------
    1         4.9400     6.8400      22.6000    31.4000      53.8000    57.2000      83.0000    84.5000
    2         4.1000     5.4000      22.4000    28.9000      58.6000    65.4000  o  106.3000   124.5000
    5         4.3000     6.5000      20.1000    26.9000      49.3000    55.6000      89.6000   107.4000
    6         3.8000     5.4000      20.6000    28.3000      56.7000    55.5000      86.4000    96.8000
    7         3.1800     4.7200      23.1000    30.9000      53.8000    63.1000      90.6000    96.6000
    8    !    4.2000!    6.7000  !   17.8000!   25.8000  o   10.8000!   47.8000  !   89.4000!   89.4000
   10         1.8000     7.3000      22.5000    29.4000      57.5000    66.0000      93.8000    89.9000
   15         5.4000     7.0000      19.0000    25.6000      46.0000    53.1000      93.6000    99.3000
   16    r    8.3000r   10.0000  r   31.1000r   36.1000  r   62.2000r   73.3000  r   90.0000r  107.0000
   17    r    6.0000r    8.0000  r   24.0000r   32.0000  r   62.0000r   68.0000  r  127.2000r  129.0000
   20         6.1000     7.5000      24.2000    29.8000      52.9000    58.4000      87.5000   103.1000
   21         4.4000     6.4000      22.2000    28.3000      50.0000    57.0000      87.4000    99.6000
   22    r   11.3000r   11.6000  r   27.1000r   34.1000  r   55.5000r   64.6000  r   96.2000r  120.8000
   24         3.8100     7.4200      22.0000    29.4000      56.2000    67.9000      87.0000   126.0000
   25         5.7000     6.9000      22.6000    27.6000      43.2000    58.4000      89.2000   107.0000
   26         5.2000     6.7000      22.0000    28.5000      50.8000    59.3000      88.7000    99.5000
   27         4.0000     7.0000      19.0000    25.0000      47.0000    54.0000      88.0000    88.0000
---------------------------------------------------------------------------------------------------------
```

```
as-5.daf

As     5   1     4.9400    6.8400   22.6000   31.4000   53.8000   57.2000   83.0000   84.5000
As     5   2     4.1000    5.4000   22.4000   28.9000   58.6000   65.4000o           124.5000
As     5   5     4.3000    6.5000   20.1000   26.9000   49.3000   55.6000   89.6000  107.4000
As     5   6     3.8000    5.4000   20.6000   28.3000   56.7000   55.5000   86.4000   96.8000
As     5   7     3.1800    4.7200   23.1000   30.9000   53.8000   63.1000   90.6000   96.6000
As     5   8     4.2000    6.7000   17.8000   25.8000o            47.8000   89.4000   89.4000
As     5  10     1.8000    7.3000   22.5000   29.4000   57.5000   66.0000   93.8000   89.9000
As     5  15     5.4000    7.0000   19.0000   25.6000   46.0000   53.1000   93.6000   99.3000
As     5  20     6.1000    7.5000   24.2000   29.8000   52.9000   58.4000   87.5000  103.1000
As     5  21     4.4000    6.4000   22.2000   28.3000   50.0000   57.0000   87.4000   99.6000
As     5  24     3.8100    7.4200   22.0000   29.4000   56.2000   67.9000   87.0000  126.0000
As     5  25     5.7000    6.9000   22.6000   27.6000   43.2000   58.4000   89.2000  107.0000
As     5  26     5.2000    6.7000   22.0000   28.5000   50.8000   59.3000   88.7000   99.5000
As     5  27     4.0000    7.0000   19.0000   25.0000   47.0000   54.0000   88.0000   88.0000
```

```
File Name:  as-5
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Reagent Grade Water
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------------------------
 ***       Results of 5x - 1/5x Mean Error Check        ***
 ***        Questionable Data (Positive Values)         ***
-------------------------------------------------------------
Total Number of Questionable Observations:     0


-------------------------------------------------------------
 ***       Results of Factor of 5 Error Check           ***
 ***         Questionable Data (All Values)             ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean                Mean    Obs
 Lev   No   No     Result     Result     Dev     Dev   Ratio
-------------------------------------------------------------
  5     8   1     50.9588    10.8000    7.013   40.159  5.73
  7    17   1     92.5823   127.2000    6.375   34.618  5.43
-------------------------------------------------------------
Total Number of Questionable Observations:     2


File Name:  as-5
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Reagent Grade Water
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
----------------------------------------------
 ***      Laboratory Ranking Results      ***
 ***   Two-Tailed 5% Significance Level   ***
 ***--------------------------------------***
 ***     Upper Critical Value:    112.0   ***
 ***     Lower Critical Value:     32.0   ***
----------------------------------------------

      Ranks
     ---------------------------------------------------------------
      Rank  Level  Level  Level  Level  Level  Level  Level  Level
Lab   Sums    1      2      3      4      5      6      7      8
---- ---------------------------------------------------------------
  1    62.0 10.00   8.00  11.50  14.00   9.50   7.00   1.00   1.00
  2    85.5  6.00   2.50   9.00   9.00  15.00  13.00  16.00  15.00
  5    54.0  8.00   5.00   4.00   4.00   5.00   5.00  10.00  13.00
  6    42.0  3.00   2.50   5.00   6.50  13.00   4.00   2.00   6.00
  7    66.5  2.00   1.00  13.00  13.00   9.50  11.00  12.00   5.00
  8    31.5  7.00   6.50   1.00   3.00   1.00   1.00   9.00   3.00
 10    79.5  1.00  12.00  10.00  10.50  14.00  14.00  14.00   4.00
 15    52.0 12.00  10.50   2.50   2.00   3.00   2.00  13.00   7.00
 16   122.5 16.00  16.00  17.00  17.00  17.00  17.00  11.00  11.50
 17   124.0 14.00  15.00  14.00  15.00  16.00  16.00  17.00  17.00
 20    87.5 15.00  14.00  15.00  12.00   8.00   8.50   5.00  10.00
 21    52.5  9.00   4.00   8.00   6.50   6.00   6.00   4.00   9.00
 22   118.0 17.00  17.00  16.00  16.00  11.00  12.00  15.00  14.00
 24    80.0  4.00  13.00   6.50  10.50  12.00  15.00   3.00  16.00
 25    68.5 13.00   9.00  11.50   5.00   2.00   8.50   8.00  11.50
 26    64.0 11.00   6.50   6.50   8.00   7.00  10.00   7.00   8.00
 27    34.0  5.00  10.50   2.50   1.00   4.00   3.00   6.00   2.00
-------------------------------------------------
 *** Laboratory  22 Rejected; Rank Sum  118.0 ***
 *** Laboratory  16 Rejected; Rank Sum  122.5 ***
 *** Laboratory  17 Rejected; Rank Sum  124.0 ***
-------------------------------------------------

File Name:  as-5
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Reagent Grade Water
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------
 ***    Outlier Testing Results      ***
 *** Two-Sided 5% Significance Level ***
-----------------------------------------

--------------------
   - Outlier(s) -
--------------------
 Lev  Iter  Lab  Rep     Result       Mean    Std Dev    t     Crit t   n
----------------------------------------------------------------------------
  5     1     8   1     10.8000    49.0429    11.9197   3.208   2.507   14
  7     1     2   1    106.3000    90.0357     5.4368   2.991   2.507   14
----------------------------------------------------------------------------
```

```
File Name:  as-5
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Reagent Grade Water
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------
 *** Results of Normality Testing ***
-------------------------------------------

-------------------------
   - Normality Tests -
-------------------------
               Test  Normality      Test           Critical
   Level  n    Type  Accept/Reject  Statistic     Value(s)
---------------------------------------------------------------
     1    14     W     A              .9561      .874   ---
     2    14     W            R       .8721      .874   ---
     3    14     W     A              .9103      .874   ---
     4    14     W     A              .9643      .874   ---
     5    13     W     A              .9617      .866   ---
     6    14     W     A              .9619      .874   ---
     7    13     W     A              .9466      .866   ---
     8    14     W     A              .8994      .874   ---
-------------------------------
 - 1 Normality Rejection(s) -
-------------------------------
```

```
File Name:  as-5
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Reagent Grade Water
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------------
 ***         Data Removal Tracking         ***
 *** Simple Count of Remaining Data Points ***
 ***          After Removal Tests          ***
-----------------------------------------------

             Points   After Lab Ranking  After Outlier Testing
               As     -----------------  ---------------------
 Lev  Mtrx  Received     Points    %        Points       %

 ---  ----  --------  ---------  ------  ----------     ------
  1     5       17           14    82.4          14       82.4
  2     5       17           14    82.4          14       82.4
  3     5       17           14    82.4          14       82.4
  4     5       17           14    82.4          14       82.4
  5     5       17           14    82.4          13       76.5
  6     5       17           14    82.4          14       82.4
  7     5       17           14    82.4          13       76.5
  8     5       17           14    82.4          14       82.4
 ---  ----  --------  ---------  ------  ----------     ------
Totals:        136         112    82.4         110       80.9
---------------------------------------------------------------
```

```
File Name:  as-5
Statistical Analysis File (.STT)


----------------------------------------
 *** Summary Performance Statistics ***
----------------------------------------
Analyte:  As         Matrix:  Reagent Grade Water
Project:  AMQ-TC     Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

----------------------------------------------------------------------------------------------------
            LEVEL:         1         2         3         4         5         6         7         8
----------------------------------------------------------------------------------------------------
YOUDEN PAIRS:         Pair 1    Pair 1    Pair 2    Pair 2    Pair 3    Pair 3    Pair 4    Pair 4
                       (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)
----------------------------------------------------------------------------------------------------
CONCENTRATION:        4.3521    6.3521   21.1521   27.5521   49.2521   57.3521   87.3521   98.6521
----------------------------------------------------------------------------------------------------
RECOVERY:
 Observations             14        14        14        14        13        14        13        14
 Mean Result          4.3521    6.5557   21.4357   28.2714   51.9846   58.4786   88.7846  100.8286
 Bias                  .0000     .2036     .2836     .7193    2.7325    1.1264    1.4325    2.1764
 Relative Bias %       .0000    3.2048    1.3406    2.6106    5.5479    1.9641    1.6399    2.2062
 Maximum Result       6.1000    7.5000   24.2000   31.4000   58.6000   67.9000   93.8000  126.0000
 Minimum Result       1.8000    4.7200   17.8000   25.0000   43.2000   47.8000   83.0000   84.5000
----------------------------------------------------------------------------------------------------
SINGLE OPERATOR PRECISION:   Pair 1              Pair 2              Pair 3              Pair 4
   Observations                  14                  14                  13                  13
   Standard Deviation         .8282               .7241              2.7448              7.9030
   Correction Factor         1.0194              1.0194              1.0210              1.0210
   Corrected Std Dev          .8443               .7381              2.8025              8.0692
   Relative Std Dev (%)     15.4798              2.9699              5.0631              8.4912
----------------------------------------------------------------------------------------------------
OVERALL PRECISION:
 Observations              14        14        14        14        13        14        13        14
 Standard Deviation    1.1002     .8273    1.8392    1.9277    4.7609    5.5420    2.8778   12.4076
 Correction Factor     1.0194    1.0194    1.0194    1.0194    1.0210    1.0194    1.0210    1.0194
 Corrected Std Dev     1.1216     .8433    1.8748    1.9651    4.8610    5.6495    2.9384   12.6483
 Relative Std Dev %   25.7701   12.8639    8.7464    6.9508    9.3509    9.6607    3.3095   12.5443
----------------------------------------------------------------------------------------------------
```

```
File Name:  as-5
Statistical Analysis File (.STT)


----------------------------------
  *** Results of Bias Testing ***
----------------------------------
 Analyte:  As         Matrix:  Reagent Grade Water
 Project:  AMQ-TC     Method:  GFAAS
    Date:  12/13/1995
   Units:  ug/L

------------------------------------------------------------------------
                                    Rel.     Obs    Crit   Statistically
Conc.             Mean              Bias       t       t     Significant
Level   Conc    Result      Bias     (%)   Value   Value   (1% Two-Tail)
------------------------------------------------------------------------
 1   4.3521    4.3521     .0000     .00    .000   3.012         NO
 2   6.3521    6.5557     .2036    3.20    .553   3.012         NO
 3  21.1521   21.4357     .2836    1.34    .495   3.012         NO
 4  27.5521   28.2714     .7193    2.61   1.213   3.012         NO
 5  49.2521   51.9846    2.7325    5.55   2.020   3.055         NO
 6  57.3521   58.4786    1.1264    1.96    .746   3.012         NO
 7  87.3521   88.7846    1.4325    1.64   1.684   3.055         NO
 8  98.6521  100.8286    2.1764    2.21    .654   3.012         NO
------------------------------------------------------------------------
```

```
File Name:  as-5
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***   Single Operator Precision    ***
----------------------------------------
Analyte:  As          Matrix:  Reagent Grade Water
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):      .5183
          Slope (b):      .0336
    =============================
                                       Single
           Sample Weights             Operator   Estimated
    Pair   Size       (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      14     71.12      5.3521       .8443       .6984
      2      14     24.14     24.3521       .7381      1.3375
      3      13      4.29     53.3021      2.8025      2.3112
      4      13       .45     93.0021      8.0692      3.6466
    -----------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    =========================================================
      a:      .5529      Intercept (a'):     -.5926
      b:     1.0288          Slope (b'):      .0284
    =========================================================
                                              Single
           Sample Weight             Operator   Estimated
    Pair   Size      (%)        Conc     Std Dev     Std Dev
    ---------------------------------------------------------
      1      14    26.02      4.3521       .8443       .6438
      2      14    26.02      6.3521       .7381      1.1050
      3      13    23.98     21.1521      2.8025      2.5170
      4      13    23.98     27.5521      8.0692      7.7831
    ---------------------------------------------------------
```

```
File Name:  as-5
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***       Overall Precision        ***
----------------------------------------
Analyte:  As          Matrix:  Reagent Grade Water
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Overall Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):      .6465
          Slope (b):      .0710
    =============================
    Conc   Sample   Weights                 Overall   Estimated
    Level  Size         (%)        Conc     Std Dev     Std Dev
    -------------------------------------------------------------
      1      14       59.11      4.3521      1.1216       .9556
      2      14       32.82      6.3521       .8433      1.0976
      3      14        3.94     21.1521      1.8748      2.1488
      4      14        2.39     27.5521      1.9651      2.6034
      5      13         .72     49.2521      4.8610      4.1446
      6      14         .58     57.3521      5.6495      4.7199
      7      13         .24     87.3521      2.9384      6.8507
      8      14         .20     98.6521     12.6483      7.6533
    -------------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    ===========================================================
      a:     1.0534      Intercept (a'):      .0520
      b:     1.0224          Slope (b'):      .0221
    ===========================================================
    Conc   Sample   Weight                 Overall   Estimated
    Level  Size        (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      14      12.75      4.3521      1.1216      1.1600
      2      14      12.75      6.3521       .8433      1.2126
      3      14      12.75     21.1521      1.8748      1.6830
      4      14      12.75     27.5521      1.9651      1.9393
      5      13      11.75     49.2521      4.8610      3.1360
      6      14      12.75     57.3521      5.6495      3.7523
      7      13      11.75     87.3521      2.9384      7.2927
      8      14      12.75     98.6521     12.6483      9.3667
    -----------------------------------------------------------
```

```
File Name:  as-5
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ************  Recovery  **************
----------------------------------------
Analyte:  As          Matrix:  Reagent Grade Water
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Recovery ***

    - Linear Model - X = b*T + a
    =============================
      Intercept (a):     -.0562
          Slope (b):     1.0269
    =============================
    Conc   Sample   Weights                 Mean   Estimated
    Level  Size         (%)      Conc      Result      Result
    ----------------------------------------------------------
      1      14     45.16      4.3521      4.3521      4.4132
      2      14     34.23      6.3521      6.5557      6.4671
      3      14      8.93     21.1521     21.4357     21.6659
      4      14      6.08     27.5521     28.2714     28.2384
      5      13      2.23     49.2521     51.9846     50.5232
      6      14      1.85     57.3521     58.4786     58.8414
      7      13       .82     87.3521     88.7846     89.6499
      8      14       .70     98.6521    100.8286    101.2544
    ----------------------------------------------------------
```

```
File Name:  as-5
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***     Precision vs Recovery      ***
----------------------------------------
Analyte:  As          Matrix:  Reagent Grade Water
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision vs Recovery ***
           (Obtained by Substitution)

     - Linear Model - s = f*X + e
    ==============================
        Intercept (e):      .5731
            Slope (f):      .0328
    ==============================


     - Curvilinear Model - s = e*(f**X)
    ====================================
        Intercept (e):      .5537
                  (f):     1.0281
    ====================================



 *** Overall Precision vs Recovery ***
       (Obtained by Substitution)

     - Linear Model - s = f*X + e
     =============================
        Intercept (e):      .7012
            Slope (f):      .0692
     =============================


     - Curvilinear Model - s = e*(f**X)
     ===================================
        Intercept (e):     1.0547
                  (f):     1.0218
     ===================================
```

```
as-8.dat

As     8   1     0.9700    0.9800    5.4200    8.9000   17.3000   23.0000   39.8000   49.8000   81.0000   83.0000
As     8   2    -1.2000   -0.6000    3.3000    6.2000   14.7000   18.9000   34.5000   42.2000   96.8000  109.9000
As     8   5     1.0000    1.1000    5.3000    9.3000   18.9000   24.2000   41.7000   51.0000   90.9000   98.7000
As     8   6    -0.6000    0.2000    4.3000    9.1000   18.0000   23.5000   40.5000   49.7000   91.8000   98.2000
As     8   7    -5.4900   -4.9500   -2.5500    3.3200   10.6000   17.8000   31.7000   39.2000   69.4000   79.0000
As     8   8     2.4000    0.0000    5.2000    9.2000   15.9000   21.7000   33.7000   38.5000   75.3000   67.5000
As     8  10    -1.7000   -2.3000   -1.3000   -1.4000   25.5000   26.2000   51.3000   58.1000   68.9000   90.2000
As     8  15     0.0000    0.6000    4.6000    8.5000   16.7000   22.1000   41.1000   51.5000   92.6000    7.9000
As     8  16    12.2000    7.2000   13.3000   18.3000   28.9000   42.8000   59.4000   64.4000   95.6000  101.0000
As     8  17     1.0000    2.0000    6.0000   10.0000   27.0000   27.0000   48.0000   56.0000  116.0000  120.0000
As     8  20     0.6000    1.5000    5.7000   11.0000   21.0000   26.3000   44.1000   95.5000   94.0000  101.5000
As     8  21     0.8000    0.6000    5.0000    8.4000   17.3000   22.5000   37.8000   44.5000   79.3000   79.6000
As     8  22    12.7000   12.7000   13.0000   14.4000   20.1000   24.6000   35.9000   42.2000   66.7000   71.6000
As     8  24     1.4900    0.0000    7.2200    8.3200   18.6000   18.5000   42.0000   40.1000   90.5000   96.9000
As     8  25     0.0000    0.0000    6.2000    9.3000   13.7000   22.6000   45.1000   44.8000   80.0000   85.6000
As     8  26     0.2000    0.3000    4.5000   10.0000   19.2000   24.6000   40.6000   51.7000   90.3000   94.9000
As     8  27    -2.0000   -2.0000    2.0000    6.0000   14.0000   20.0000   36.0000   45.0000   81.0000   97.0000
```

```
File Name:  as-5
Data Validation File (.DA~)

******************************************************************************
***                   Parameter and Data Validation File                   ***
******************************************************************************
   Analyte:  As              Matrix:  Reagent Grade Water
   Project:  AMQ-TC       Matrix ID:   5
      Date:  12/13/1995      Method:  GFAAS
     Pairs:  4
     Units:  ug/L

---------------------------------------------------------------------------------------------------------
Level          1          2            3          4            5          6            7          8
---------------------------------------------------------------------------------------------------------
Spike         4.3521     2.0000      14.8000     6.4000      21.7000     8.1000      30.0000    11.3000
Spike
Increment      .0000     2.0000      16.8000    23.2000      44.9000    53.0000      83.0000    94.3000
---------------------------------------------------------------------------------------------------------

                 Final Concentration
         ------------------------------------------------------------------------------------------------
Lab ID        4.3521     6.3521      21.1521    27.5521      49.2521    57.3521      87.3521    98.6521
---------------------------------------------------------------------------------------------------------
    1         4.9400     6.8400      22.6000    31.4000      53.8000    57.2000      83.0000    84.5000
    2         4.1000     5.4000      22.4000    28.9000      58.6000    65.4000   o  106.3000   124.5000
    5         4.3000     6.5000      20.1000    26.9000      49.3000    55.6000      89.6000   107.4000
    6         3.8000     5.4000      20.6000    28.3000      56.7000    55.5000      86.4000    96.8000
    7         3.1800     4.7200      23.1000    30.9000      53.8000    63.1000      90.6000    96.6000
    8    !    4.2000!    6.7000  !   17.8000!   25.8000  o   10.8000!   47.8000  !   89.4000!   89.4000
   10         1.8000     7.3000      22.5000    29.4000      57.5000    66.0000      93.8000    89.9000
   15         5.4000     7.0000      19.0000    25.6000      46.0000    53.1000      93.6000    99.3000
   16    r    8.3000r   10.0000  r   31.1000r   36.1000  r   62.2000r   73.3000  r   90.0000r  107.0000
   17    r    6.0000r    8.0000  r   24.0000r   32.0000  r   62.0000r   68.0000  r  127.2000r  129.0000
   20         6.1000     7.5000      24.2000    29.8000      52.9000    58.4000      87.5000   103.1000
   21         4.4000     6.4000      22.2000    28.3000      50.0000    57.0000      87.4000    99.6000
   22    r   11.3000r   11.6000  r   27.1000r   34.1000  r   55.5000r   64.6000  r   96.2000r  120.8000
   24         3.8100     7.4200      22.0000    29.4000      56.2000    67.9000      87.0000   126.0000
   25         5.7000     6.9000      22.6000    27.6000      43.2000    58.4000      89.2000   107.0000
   26         5.2000     6.7000      22.0000    28.5000      50.8000    59.3000      88.7000    99.5000
   27         4.0000     7.0000      19.0000    25.0000      47.0000    54.0000      88.0000    88.0000
---------------------------------------------------------------------------------------------------------
```

```
as-8.daf

As     8   1      .9700     .9800    5.4200    8.9000   17.3000   23.0000   39.8000   49.8000   81.0000   83.0000
As     8   2    -1.2000    -.6000    3.3000    6.2000   14.7000   18.9000   34.5000   42.2000   96.8000  109.9000
As     8   5     1.0000    1.1000    5.3000    9.3000   18.9000   24.2000   41.7000   51.0000   90.9000   98.7000
As     8   6     -.6000     .2000    4.3000    9.1000   18.0000   23.5000   40.5000   49.7000   91.8000   98.2000
As     8   8     2.4000     .0000    5.2000    9.2000   15.9000   21.7000   33.7000   38.5000   75.3000   67.5000
As     8  10    -1.7000   -2.3000   -1.3000o            25.5000   26.2000   51.3000   58.1000   68.9000   90.2000
As     8  15      .0000     .6000    4.6000    8.5000   16.7000   22.1000   41.1000   51.5000   92.6000o
As     8  20      .6000    1.5000    5.7000   11.0000   21.0000   26.3000   44.1000o            94.0000  101.5000
As     8  21      .8000     .6000    5.0000    8.4000   17.3000   22.5000   37.8000   44.5000   79.3000   79.6000
As     8  22 o         o         o            14.4000   20.1000   24.6000   35.9000   42.2000   66.7000   71.6000
As     8  24     1.4900     .0000    7.2200    8.3200   18.6000   18.5000   42.0000   40.1000   90.5000   96.9000
As     8  25      .0000     .0000    6.2000    9.3000   13.7000   22.6000   45.1000   44.8000   80.0000   85.6000
As     8  26      .2000     .3000    4.5000   10.0000   19.2000   24.6000   40.6000   51.7000   90.3000   94.9000
As     8  27    -2.0000   -2.0000    2.0000    6.0000   14.0000   20.0000   36.0000   45.0000   81.0000   97.0000
```

```
File Name:  as-8
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Freshwater
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------------------------
 ***        Results of 5x - 1/5x Mean Error Check        ***
 ***         Questionable Data (Positive Values)         ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean
 Lev   No   No     Result     Result                   Ratio
-------------------------------------------------------------
  1     16  1      1.9624    12.2000                  6.22
  1     22  1      1.9624    12.7000                  6.47
  1     26  1      1.9624      .2000                   .10
  2      6  1      1.5988      .2000                   .13
  2     22  1      1.5988    12.7000                  7.94
  2     26  1      1.5988      .3000                   .19
 10     15  1     87.2059     7.9000                   .09
-------------------------------------------------------------
Total Number of Questionable Observations:     7


-------------------------------------------------------------
 ***        Results of Factor of 5 Error Check           ***
 ***         Questionable Data (All Values)              ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean                 Mean    Obs
 Lev   No   No     Result     Result     Dev     Dev   Ratio
-------------------------------------------------------------
  2    22   1      1.0194    12.7000    2.283   11.681  5.12
  6    16   1     23.9000    42.8000    3.341   18.900  5.66
  8    20   1     50.8353    95.5000    8.512   44.665  5.25
-------------------------------------------------------------
Total Number of Questionable Observations:     3


File Name:  as-8
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Freshwater
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
----------------------------------------------
 ***      Laboratory Ranking Results      ***
 ***   Two-Tailed 5% Significance Level   ***
 ***--------------------------------------***
 ***     Upper Critical Value:    135.0   ***
 ***     Lower Critical Value:     45.0   ***
----------------------------------------------

      Ranks
     -----------------------------------------------------------------------------
       Rank  Level  Level  Level  Level  Level  Level  Level  Level  Level  Level
Lab    Sums    1      2      3      4      5      6      7      8      9      10
---- -----------------------------------------------------------------------------
  1    89.0  11.00  12.00  11.00   8.00   7.50   9.00   7.00  10.00   7.50   6.00
  2    62.5   4.00   4.00   4.00   4.00   4.00   3.00   3.00   4.50  16.00  16.00
  5   115.0  12.50  13.00  10.00  11.50  11.00  11.00  11.00  11.00  11.00  13.00
  6    87.0   5.00   8.00   5.00   9.00   9.00  10.00   8.00   9.00  12.00  12.00
  7    17.0   1.00   1.00   1.00   2.00   1.00   1.00   1.00   2.00   3.00   4.00
  8    59.0  15.00   6.00   9.00  10.00   5.00   5.00   2.00   1.00   4.00   2.00
 10    78.0   3.00   2.00   2.00   1.00  15.00  14.00  16.00  15.00   2.00   8.00
 15    79.0   6.50  10.50   7.00   7.00   6.00   6.00  10.00  12.00  13.00   1.00
 16   162.0  16.00  16.00  17.00  17.00  17.00  17.00  17.00  16.00  15.00  14.00
 17   149.0  12.50  15.00  13.00  13.50  16.00  16.00  15.00  14.00  17.00  17.00
 20   138.0   9.00  14.00  12.00  15.00  14.00  15.00  13.00  17.00  14.00  15.00
 21    71.0  10.00  10.50   8.00   6.00   7.50   7.00   6.00   6.00   5.00   5.00
 22   104.0  17.00  17.00  16.00  16.00  13.00  12.50   4.00   4.50   1.00   3.00
 24    87.0  14.00   6.00  15.00   5.00  10.00   2.00  12.00   3.00  10.00  10.00
 25    82.0   6.50   6.00  14.00  11.50   2.00   8.00  14.00   7.00   6.00   7.00
 26   101.0   8.00   9.00   6.00  13.50  12.00  12.50   9.00  13.00   9.00   9.00
 27    49.5   2.00   3.00   3.00   3.00   3.00   4.00   5.00   8.00   7.50  11.00
-------------------------------------------------
 *** Laboratory  17 Rejected; Rank Sum  149.0 ***
 *** Laboratory  16 Rejected; Rank Sum  162.0 ***
 *** Laboratory   7 Rejected; Rank Sum   17.0 ***
-------------------------------------------------
```

```
File Name:  as-8
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Freshwater
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------
 ***    Outlier Testing Results      ***
 *** Two-Sided 5% Significance Level ***
-----------------------------------------

--------------------
   - Outlier(s) -
--------------------
 Lev  Iter  Lab  Rep     Result       Mean    Std Dev    t     Crit t   n
-----------------------------------------------------------------------------
  1     1    22   1     12.7000     1.0471     3.5690   3.265   2.507   14
  2     1    22   1     12.7000      .9343     3.5517   3.313   2.507   14
  3     1    22   1     13.0000     5.0314     3.0838   2.584   2.507   14
  4     1    10   1     -1.4000     8.3729     3.4526   2.831   2.507   14
  8     1    20   1     95.5000    50.3286    14.0736   3.210   2.507   14
  *     1    15   1      7.9000    84.4643    24.9993   3.063   2.507   14
-----------------------------------------------------------------------------
```

```
File Name:  as-8
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Freshwater
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------
 *** Results of Normality Testing ***
-------------------------------------------

-------------------------
   - Normality Tests -
-------------------------
               Test  Normality      Test          Critical
   Level  n    Type  Accept/Reject  Statistic     Value(s)
---------------------------------------------------------------
     1    13     W     A               .9720      .866   ---
     2    13     W     A               .8852      .866   ---
     3    13     W            R        .8500      .866   ---
     4    13     W     A               .8771      .866   ---
     5    14     W     A               .9403      .874   ---
     6    14     W     A               .9523      .874   ---
     7    14     W     A               .9459      .874   ---
     8    13     W     A               .9517      .866   ---
     9    14     W     A               .9126      .874   ---
    10    13     W     A               .9498      .866   ---
-------------------------------
 - 1 Normality Rejection(s) -
-------------------------------
```

```
File Name:  as-8
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Freshwater
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------------
 ***         Data Removal Tracking         ***
 *** Simple Count of Remaining Data Points ***
 ***          After Removal Tests          ***
-----------------------------------------------

             Points   After Lab Ranking  After Outlier Testing
               As     -----------------  ---------------------
 Lev  Mtrx  Received     Points    %         Points       %

 ---  ----  --------  ---------  ------  ----------     ------
  1     8       17          14    82.4          13       76.5
  2     8       17          14    82.4          13       76.5
  3     8       17          14    82.4          13       76.5
  4     8       17          14    82.4          13       76.5
  5     8       17          14    82.4          14       82.4
  6     8       17          14    82.4          14       82.4
  7     8       17          14    82.4          14       82.4
  8     8       17          14    82.4          13       76.5
  9     8       17          14    82.4          14       82.4
 10     8       17          14    82.4          13       76.5
 ---  ----  --------  ---------  ------  ----------     ------
Totals:       170         140    82.4         134       78.8
--------------------------------------------------------------
```

```
File Name:  as-8
Statistical Analysis File (.STT)


----------------------------------------
 *** Summary Performance Statistics ***
----------------------------------------
Analyte:  As          Matrix:  Freshwater
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

------------------------------------------------------------------------------------------------------------------------
            LEVEL:         1         2         3         4         5         6         7         8         9        10
------------------------------------------------------------------------------------------------------------------------
YOUDEN PAIRS:          Pair 1    Pair 1    Pair 2    Pair 2    Pair 3    Pair 3    Pair 4    Pair 4    Pair 5    Pair 5
                        (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)
------------------------------------------------------------------------------------------------------------------------
CONCENTRATION:          .0900     .0900    4.2900    8.1900   17.2900   22.2900   38.9900   47.4900   85.1900   91.2900
------------------------------------------------------------------------------------------------------------------------
RECOVERY:
 Observations              13        13        13        13        14        14        14        13        14        13
 Mean Result            .1508     .0292    4.4185    9.1246   17.9214   22.7643   40.2929   46.8538   84.2214   90.3538
 Bias                   .0608    -.0608     .1285     .9346     .6314     .4743    1.3029    -.6362    -.9686    -.9362
 Relative Bias %      67.5214  -67.5214    2.9944   11.4117    3.6520    2.1278    3.3415   -1.3396   -1.1370   -1.0255
 Maximum Result        2.4000    1.5000    7.2200   14.4000   25.5000   26.3000   51.3000   58.1000   96.8000  109.9000
 Minimum Result       -2.0000   -2.3000   -1.3000    6.0000   13.7000   18.5000   33.7000   38.5000   66.7000   67.5000
------------------------------------------------------------------------------------------------------------------------
SINGLE OPERATOR PRECISION:   Pair 1              Pair 2              Pair 3              Pair 4              Pair 5
   Observations                  13                  12                  14                  13                  13
   Standard Deviation         .6576               .8291              1.5588              2.8112              5.1020
   Correction Factor         1.0210              1.0230              1.0194              1.0210              1.0210
   Corrected Std Dev          .6714               .8481              1.5890              2.8703              5.2093
   Relative Std Dev (%)    746.0185             12.5242              7.8112              6.6058              5.9757
------------------------------------------------------------------------------------------------------------------------
OVERALL PRECISION:
 Observations               13        13        13        13        14        14        14        13        14        13
 Standard Deviation     1.2700    1.1146    2.1457    2.0839    3.0964    2.4200    4.6876    5.6082    9.5539   12.2867
 Correction Factor      1.0210    1.0210    1.0210    1.0210    1.0194    1.0194    1.0194    1.0210    1.0194    1.0210
 Corrected Std Dev      1.2967    1.1381    2.1908    2.1277    3.1565    2.4669    4.7785    5.7262    9.7392   12.5450
 Relative Std Dev %   860.0747 3893.4530   49.5833   23.3182   17.6130   10.8368   11.8594   12.2213   11.5638   13.8843
------------------------------------------------------------------------------------------------------------------------
```

```
File Name:  as-8
Statistical Analysis File (.STT)


----------------------------------
  *** Results of Bias Testing ***
----------------------------------
 Analyte:  As          Matrix:  Freshwater
 Project:  AMQ-TC      Method:  GFAAS
    Date:  12/13/1995
   Units:  ug/L

------------------------------------------------------------------------
                                    Rel.   Obs    Crit   Statistically
Conc.             Mean              Bias     t       t     Significant
Level   Conc    Result      Bias     (%)  Value   Value   (1% Two-Tail)
------------------------------------------------------------------------
 1     .0900     .1508     .0608   67.52  .172     3.055         NO
 2     .0900     .0292    -.0608  -67.52  .197     3.055         NO
 3    4.2900    4.4185     .1285    2.99  .216     3.055         NO
 4    8.1900    9.1246     .9346   11.41 1.617     3.055         NO
 5   17.2900   17.9214     .6314    3.65  .763     3.012         NO
 6   22.2900   22.7643     .4743    2.13  .733     3.012         NO
 7   38.9900   40.2929    1.3029    3.34 1.040     3.012         NO
 8   47.4900   46.8538    -.6362   -1.34  .409     3.055         NO
 9   85.1900   84.2214    -.9686   -1.14  .379     3.012         NO
10   91.2900   90.3538    -.9362   -1.03  .275     3.055         NO
------------------------------------------------------------------------
```

```
File Name:  as-8
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***   Single Operator Precision    ***
----------------------------------------
Analyte:  As          Matrix:  Freshwater
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):      .6307
          Slope (b):      .0501
    =============================
                                           Single
           Sample Weights               Operator   Estimated
    Pair   Size       (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      13     63.04       .0900       .6714       .6352
      2      12     24.27      6.2400       .8481       .9433
      3      14      9.14     19.7900      1.5890      1.6220
      4      13      2.73     43.2400      2.8703      2.7967
      5      13       .82     88.2400      5.2093      5.0508
    -----------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    =========================================================
      a:      .8248      Intercept (a'):     -.1927
      b:     1.0231          Slope (b'):      .0228
    =========================================================
                                                  Single
           Sample Weight               Operator   Estimated
    Pair   Size      (%)        Conc     Std Dev     Std Dev
    ---------------------------------------------------------
      1      13    20.00       .0900       .6714       .8265
      2      12    18.30       .0900       .8481       .9509
      3      14    21.70      4.2900      1.5890      1.2954
      4      13    20.00      8.1900      2.8703      2.2116
      5      13    20.00     17.2900      5.2093      6.1736
    ---------------------------------------------------------
```

```
File Name:  as-8
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***       Overall Precision        ***
----------------------------------------
Analyte:  As          Matrix:  Freshwater
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Overall Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):     1.2859
          Slope (b):      .0992
    =============================
    Conc   Sample   Weights                 Overall   Estimated
    Level  Size        (%)        Conc     Std Dev     Std Dev
    -------------------------------------------------------------
      1      13       32.68       .0900      1.2967      1.2948
      2      13       32.68       .0900      1.1381      1.2948
      3      13       15.37      4.2900      2.1908      1.7116
      4      13        9.21      8.1900      2.1277      2.0986
      5      14        4.28     17.2900      3.1565      3.0016
      6      14        3.03     22.2900      2.4669      3.4977
      7      14        1.29     38.9900      4.7785      5.1549
      8      13         .86     47.4900      5.7262      5.9983
      9      14         .34     85.1900      9.7392      9.7393
     10      13         .27     91.2900     12.5450     10.3446
    -------------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    ===========================================================
      a:     1.6314      Intercept (a'):      .4895
      b:     1.0232          Slope (b'):      .0229
    ===========================================================
    Conc   Sample   Weight                 Overall   Estimated
    Level  Size        (%)       Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      13        9.67       .0900      1.2967      1.6348
      2      13        9.67       .0900      1.1381      1.6348
      3      13        9.67      4.2900      2.1908      1.7998
      4      13        9.67      8.1900      2.1277      1.9679
      5      14       10.49     17.2900      3.1565      2.4238
      6      14       10.49     22.2900      2.4669      2.7178
      7      14       10.49     38.9900      4.7785      3.9835
      8      13        9.67     47.4900      5.7262      4.8394
      9      14       10.49     85.1900      9.7392     11.4725
     10      13        9.67     91.2900     12.5450     13.1921
    -----------------------------------------------------------
```

```
File Name:  as-8
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ************  Recovery  **************
----------------------------------------
Analyte:  As          Matrix:  Freshwater
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Recovery ***

    - Linear Model - X = b*T + a
    =============================
      Intercept (a):      .1635
          Slope (b):     1.0043
    =============================
    Conc   Sample   Weights                  Mean   Estimated
    Level  Size         (%)      Conc      Result      Result
    ----------------------------------------------------------
      1      13     28.98       .0900       .1508       .2539
      2      13     28.98       .0900       .0292       .2539
      3      13     16.59      4.2900      4.4185      4.4719
      4      13     11.03      8.1900      9.1246      8.3886
      5      14      5.81     17.2900     17.9214     17.5277
      6      14      4.28     22.2900     22.7643     22.5491
      7      14      1.97     38.9900     40.2929     39.3208
      8      13      1.35     47.4900     46.8538     47.8572
      9      14       .55     85.1900     84.2214     85.7190
     10      13       .45     91.2900     90.3538     91.8452
    ----------------------------------------------------------


File Name:  as-8
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***     Precision vs Recovery      ***
----------------------------------------
Analyte:  As          Matrix:  Freshwater
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision vs Recovery ***
           (Obtained by Substitution)

     - Linear Model - s = f*X + e
    ==============================
        Intercept (e):      .4680
            Slope (f):      .0499
    ==============================


     - Curvilinear Model - s = e*(f**X)
    ====================================
        Intercept (e):      .8217
                  (f):     1.0230
    ====================================



 *** Overall Precision vs Recovery ***
       (Obtained by Substitution)

     - Linear Model - s = f*X + e
     =============================
        Intercept (e):     1.1231
            Slope (f):      .0988
     =============================


     - Curvilinear Model - s = e*(f**X)
     ===================================
        Intercept (e):     1.6254
                  (f):     1.0231
     ===================================
```

```
as-9.dat

As     9   5    14.0000   13.0000   58.0000   70.0000  254.0000  313.0000  614.0000  677.0000  907.0000  974.0000
As     9   6    -4.0000   -3.0000   48.0000   48.0000  219.0000  255.0000  561.0000  611.0000  799.0000  929.0000
As     9   7    -2.1500    2.2600   22.2000   23.3000  163.0000  172.0000  437.0000  470.0000  641.0000  618.0000
As     9   8     3.0000    0.2000   48.4000   65.7000  238.0000  318.0000  422.0000  384.0000  864.0000  760.0000
As     9  10     5.7000   19.5000   36.0000    1.0000  228.0000  213.0000  487.0000  727.0000  727.0000 1040.0000
As     9  15     4.2000    2.7000   32.0000   42.0000  185.0000  242.0000  494.0000  568.0000  749.0000  820.0000
As     9  16    60.0000   60.0000  167.0000   66.0000  367.0000  254.0000  722.0000  833.0000  723.0000  888.0000
As     9  17     3.0000    3.0000   48.0000   58.0000  261.0000  280.0000  560.0000  620.0000  840.0000  880.0000
As     9  20    26.0000   20.0000   67.0000   67.0000  275.0000  320.0000  664.0000  657.0000  896.0000  969.0000
As     9  21     3.0000    2.7000   44.5000   55.0000  220.0000  269.0000  532.0000  578.0000  791.0000  835.0000
As     9  22    14.0000   16.5000   51.9000   66.2000  269.0000  311.0000  491.0000  562.0000  848.0000  793.0000
As     9  24     6.0000    6.2000   47.1000   55.0000  152.0000  168.0000  318.0000  718.0000  919.0000 1167.0000
As     9  25     3.2000    3.2000   42.9000   56.1000  240.0000  267.0000  594.0000  535.0000  861.0000  939.0000
As     9  26    -6.0000   10.0000   54.0000   55.0000  251.0000  313.0000  603.0000  677.0000  831.0000  924.0000
As     9  27   -20.0000  -30.0000   20.0000   30.0000  190.0000  240.0000  530.0000  530.0000  770.0000  770.0000
```

```
File Name:  as-9
Data Validation File (.DA~)

******************************************************************************
***                   Parameter and Data Validation File                   ***
******************************************************************************
   Analyte:  As              Matrix:  Estuarine
   Project:  AMQ-TC       Matrix ID:   9
      Date:  12/13/1995      Method:  GFAAS
     Pairs:  5
     Units:  ug/L

--------------------------------------------------------------------------------------------------------------------------------
Level          1          2            3          4            5          6            7          8            9         10
--------------------------------------------------------------------------------------------------------------------------------
Spike          5.4590      .0000      44.9000    11.4000     167.0000    53.0000     270.0000    49.0000     199.0000    59.0000
Spike
Increment       .0000      .0000      44.9000    56.3000     223.3000   276.3000     546.3000   595.3000     794.3000   853.3000
--------------------------------------------------------------------------------------------------------------------------------

                 Final Concentration
         -----------------------------------------------------------------------------------------------------------------------
Lab ID         5.4590     5.4590      50.3590    61.7590     228.7590   281.7590     551.7590   600.7590     799.7590   858.7590
--------------------------------------------------------------------------------------------------------------------------------
     5   !    14.0000!   13.0000 !    58.0000!   70.0000 !   254.0000!  313.0000 !   614.0000!  677.0000 !   907.0000!  974.0000
     6        -4.0000    -3.0000      48.0000    48.0000     219.0000   255.0000     561.0000   611.0000     799.0000   929.0000
     7   r    -2.1500r    2.2600 r    22.2000r   23.3000 r   163.0000r  172.0000 r   437.0000r  470.0000 r   641.0000r  618.0000
     8         3.0000      .2000      48.4000    65.7000     238.0000   318.0000     422.0000   384.0000     864.0000   760.0000
    10         5.7000    19.5000      36.0000o    1.0000     228.0000   213.0000     487.0000   727.0000     727.0000  1040.0000
    15         4.2000     2.7000      32.0000    42.0000     185.0000   242.0000     494.0000   568.0000     749.0000   820.0000
    16   o    60.0000o   60.0000 o   167.0000    66.0000 o   367.0000   254.0000     722.0000   833.0000     723.0000   888.0000
    17         3.0000     3.0000      48.0000    58.0000     261.0000   280.0000     560.0000   620.0000     840.0000   880.0000
    20   r    26.0000r   20.0000 r    67.0000r   67.0000 r   275.0000r  320.0000 r   664.0000r  657.0000 r   896.0000r  969.0000
    21         3.0000     2.7000      44.5000    55.0000     220.0000   269.0000     532.0000   578.0000     791.0000   835.0000
    22        14.0000    16.5000      51.9000    66.2000     269.0000   311.0000     491.0000   562.0000     848.0000   793.0000
    24         6.0000     6.2000      47.1000    55.0000     152.0000   168.0000     318.0000   718.0000     919.0000  1167.0000
    25         3.2000     3.2000      42.9000    56.1000     240.0000   267.0000     594.0000   535.0000     861.0000   939.0000
    26        -6.0000    10.0000      54.0000    55.0000     251.0000   313.0000     603.0000   677.0000     831.0000   924.0000
    27   r   -20.0000r  -30.0000 r    20.0000r   30.0000 r   190.0000r  240.0000 r   530.0000r  530.0000 r   770.0000r  770.0000
--------------------------------------------------------------------------------------------------------------------------------
```

```
as-9.daf

As     9   5    14.0000   13.0000   58.0000   70.0000  254.0000  313.0000  614.0000  677.0000  907.0000  974.0000
As     9   6    -4.0000   -3.0000   48.0000   48.0000  219.0000  255.0000  561.0000  611.0000  799.0000  929.0000
As     9   8     3.0000     .2000   48.4000   65.7000  238.0000  318.0000  422.0000  384.0000  864.0000  760.0000
As     9  10     5.7000   19.5000   36.0000o           228.0000  213.0000  487.0000  727.0000  727.0000 1040.0000
As     9  15     4.2000    2.7000   32.0000   42.0000  185.0000  242.0000  494.0000  568.0000  749.0000  820.0000
As     9  16 o         o         o            66.0000o           254.0000  722.0000  833.0000  723.0000  888.0000
As     9  17     3.0000    3.0000   48.0000   58.0000  261.0000  280.0000  560.0000  620.0000  840.0000  880.0000
As     9  21     3.0000    2.7000   44.5000   55.0000  220.0000  269.0000  532.0000  578.0000  791.0000  835.0000
As     9  22    14.0000   16.5000   51.9000   66.2000  269.0000  311.0000  491.0000  562.0000  848.0000  793.0000
As     9  24     6.0000    6.2000   47.1000   55.0000  152.0000  168.0000  318.0000  718.0000  919.0000 1167.0000
As     9  25     3.2000    3.2000   42.9000   56.1000  240.0000  267.0000  594.0000  535.0000  861.0000  939.0000
As     9  26    -6.0000   10.0000   54.0000   55.0000  251.0000  313.0000  603.0000  677.0000  831.0000  924.0000
```

```
File Name:  as-9
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Estuarine
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------------------------
 ***       Results of 5x - 1/5x Mean Error Check        ***
 ***        Questionable Data (Positive Values)         ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean
 Lev   No   No     Result     Result                   Ratio
-------------------------------------------------------------
   1     16  1      9.4733    60.0000                  6.33
   2      8  1     10.6173      .2000                   .02
   2     16  1     10.6173    60.0000                  5.65
   4     10  1     50.5533     1.0000                   .02
-------------------------------------------------------------
Total Number of Questionable Observations:     4


-------------------------------------------------------------
 ***       Results of Factor of 5 Error Check           ***
 ***         Questionable Data (All Values)             ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean                 Mean    Obs
 Lev   No   No     Result     Result     Dev     Dev   Ratio
-------------------------------------------------------------
   3    16   1     52.4667   167.0000   18.151  114.533  6.31
-------------------------------------------------------------
Total Number of Questionable Observations:     1


File Name:  as-9
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Estuarine
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
----------------------------------------------
 ***      Laboratory Ranking Results      ***
 ***   Two-Tailed 5% Significance Level   ***
 ***--------------------------------------***
 ***     Upper Critical Value:    119.0   ***
 ***     Lower Critical Value:     40.0   ***
----------------------------------------------

      Ranks
     ----------------------------------------------------------------------------
       Rank  Level  Level  Level  Level  Level  Level  Level  Level  Level  Level
Lab    Sums    1      2      3      4      5      6      7      8      9     10
---- ----------------------------------------------------------------------------
  5   126.5  12.50  11.00  13.00  15.00  11.00  12.50  13.00  11.50  14.00  13.00
  6    65.5   3.00   2.00   8.50   5.00   5.00   7.00  10.00   8.00   7.00  10.00
  7    23.0   4.00   4.00   2.00   2.00   2.00   2.00   3.00   2.00   1.00   1.00
  8    69.0   6.00   3.00  10.00  11.00   8.00  14.00   2.00   1.00  12.00   2.00
 10    73.0  10.00  13.00   4.00   1.00   7.00   3.00   4.00  14.00   3.00  14.00
 15    50.5   9.00   5.50   3.00   4.00   3.00   5.00   6.00   6.00   4.00   5.00
 16   118.0  15.00  15.00  15.00  12.00  15.00   6.00  15.00  15.00   2.00   8.00
 17    87.5   6.00   7.00   8.50  10.00  12.00  10.00   9.00   9.00   9.00   7.00
 20   134.0  14.00  14.00  14.00  14.00  14.00  15.00  14.00  10.00  13.00  12.00
 21    66.5   6.00   5.50   6.00   7.00   6.00   9.00   8.00   7.00   6.00   6.00
 22    96.5  12.50  12.00  11.00  13.00  13.00  11.00   5.00   5.00  10.00   4.00
 24    80.0  11.00   9.00   7.00   7.00   1.00   1.00   1.00  13.00  15.00  15.00
 25    84.0   8.00   8.00   5.00   9.00   9.00   8.00  11.00   4.00  11.00  11.00
 26    94.0   2.00  10.00  12.00   7.00  10.00  12.50  12.00  11.50   8.00   9.00
 27    32.0   1.00   1.00   1.00   3.00   4.00   4.00   7.00   3.00   5.00   3.00
-------------------------------------------------
 *** Laboratory  27 Rejected; Rank Sum   32.0 ***
 *** Laboratory  20 Rejected; Rank Sum  134.0 ***
 *** Laboratory   7 Rejected; Rank Sum   23.0 ***
-------------------------------------------------

File Name:  as-9
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Estuarine
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------
 ***    Outlier Testing Results      ***
 *** Two-Sided 5% Significance Level ***
-----------------------------------------

--------------------
   - Outlier(s) -
--------------------
 Lev  Iter  Lab  Rep     Result       Mean    Std Dev    t     Crit t   n
----------------------------------------------------------------------------
   1     1    16   1     60.0000     8.8417    17.1339   2.986   2.412   12
   2     1    16   1     60.0000    11.1667    16.8049   2.906   2.412   12
   3     1    16   1    167.0000    56.4833    35.5321   3.110   2.412   12
   4     1    10   1      1.0000    53.1667    18.3149   2.848   2.412   12
   5     1    16   1    367.0000   240.3333    51.7728   2.447   2.412   12
----------------------------------------------------------------------------
```

```
File Name:  as-9
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Estuarine
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------
 *** Results of Normality Testing ***
-------------------------------------------

-------------------------
   - Normality Tests -
-------------------------
               Test  Normality      Test          Critical
   Level  n    Type  Accept/Reject  Statistic     Value(s)
---------------------------------------------------------------
     1    11     W     A              .8966      .850   ---
     2    11     W     A              .9238      .850   ---
     3    11     W     A              .9537      .850   ---
     4    11     W     A              .9332      .850   ---
     5    11     W     A              .9010      .850   ---
     6    12     W     A              .9106      .859   ---
     7    12     W     A              .9680      .859   ---
     8    12     W     A              .9691      .859   ---
     9    12     W     A              .9459      .859   ---
    10    12     W     A              .9445      .859   ---
-------------------------------
 - 0 Normality Rejection(s) -
-------------------------------
```

```
File Name:  as-9
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Estuarine
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------------
 ***         Data Removal Tracking         ***
 *** Simple Count of Remaining Data Points ***
 ***          After Removal Tests          ***
-----------------------------------------------

             Points   After Lab Ranking  After Outlier Testing
               As     -----------------  ---------------------
 Lev  Mtrx  Received     Points    %         Points       %

 ---  ----  --------  ---------  ------  ----------     ------
  1     9       15          12    80.0          11       73.3
  2     9       15          12    80.0          11       73.3
  3     9       15          12    80.0          11       73.3
  4     9       15          12    80.0          11       73.3
  5     9       15          12    80.0          11       73.3
  6     9       15          12    80.0          12       80.0
  7     9       15          12    80.0          12       80.0
  8     9       15          12    80.0          12       80.0
  9     9       15          12    80.0          12       80.0
 10     9       15          12    80.0          12       80.0
 ---  ----  --------  ---------  ------  ----------     ------
Totals:        150         120    80.0         115       76.7
--------------------------------------------------------------
```

```
File Name:  as-9
Statistical Analysis File (.STT)


----------------------------------------
 *** Summary Performance Statistics ***
----------------------------------------
Analyte:  As          Matrix:  Estuarine
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

------------------------------------------------------------------------------------------------------------------------
            LEVEL:         1         2         3         4         5         6         7         8         9        10
------------------------------------------------------------------------------------------------------------------------
YOUDEN PAIRS:         Pair 1    Pair 1    Pair 2    Pair 2    Pair 3    Pair 3    Pair 4    Pair 4    Pair 5    Pair 5
                       (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)
------------------------------------------------------------------------------------------------------------------------
CONCENTRATION:        5.4590    5.4590   50.3590   61.7590  228.7590  281.7590  551.7590  600.7590  799.7590  858.7590
------------------------------------------------------------------------------------------------------------------------
RECOVERY:
 Observations             11        11        11        11        11        12        12        12        12        12
 Mean Result          4.1909    6.7273   46.4364   57.9091  228.8182  266.9167  533.1667  624.1667  821.5833  912.4167
 Bias                -1.2681    1.2683   -3.9226   -3.8499     .0592  -14.8423  -18.5924   23.4076   21.8243   53.6576
 Relative Bias %    -23.2294   23.2327   -7.7893   -6.2338     .0259   -5.2677   -3.3697    3.8963    2.7289    6.2483
 Maximum Result      14.0000   19.5000   58.0000   70.0000  269.0000  318.0000  722.0000  833.0000  919.0000 1167.0000
 Minimum Result      -6.0000   -3.0000   32.0000   42.0000  152.0000  168.0000  318.0000  384.0000  723.0000  760.0000
------------------------------------------------------------------------------------------------------------------------
SINGLE OPERATOR PRECISION:   Pair 1              Pair 2              Pair 3              Pair 4              Pair 5
   Observations                  11                  10                  11                  12                  12
   Standard Deviation        4.4393              3.8747             18.7619             86.2481             81.5279
   Correction Factor         1.0253              1.0281              1.0253              1.0230              1.0230
   Corrected Std Dev         4.5515              3.9836             19.2361             88.2279             83.3995
   Relative Std Dev (%)     83.3743              7.6354              7.7348             15.2468              9.6193
------------------------------------------------------------------------------------------------------------------------
OVERALL PRECISION:
 Observations              11        11        11        11        11        12        12        12        12        12
 Standard Deviation    6.1169    7.1062    7.5070    8.4914   34.6145   45.3240  102.8519  114.2349   65.1173  112.6825
 Correction Factor     1.0253    1.0253    1.0253    1.0253    1.0253    1.0230    1.0230    1.0230    1.0230    1.0230
 Corrected Std Dev     6.2715    7.2858    7.6967    8.7060   35.4893   46.3644  105.2130  116.8572   66.6121  115.2693
 Relative Std Dev %  149.6460  108.3025   16.5747   15.0340   15.5098   17.3704   19.7336   18.7221    8.1078   12.6334
------------------------------------------------------------------------------------------------------------------------
```

```
File Name:  as-9
Statistical Analysis File (.STT)


----------------------------------
  *** Results of Bias Testing ***
----------------------------------
 Analyte:  As          Matrix:  Estuarine
 Project:  AMQ-TC      Method:  GFAAS
    Date:  12/13/1995
   Units:  ug/L

------------------------------------------------------------------------
                                    Rel.    Obs     Crit   Statistically
Conc.             Mean              Bias      t        t     Significant
Level   Conc    Result      Bias     (%)   Value   Value   (1% Two-Tail)
------------------------------------------------------------------------
 1    5.4590    4.1909   -1.2681  -23.23    .689   3.169         NO
 2    5.4590    6.7273    1.2683   23.23    .592   3.169         NO
 3   50.3590   46.4364   -3.9226   -7.79   1.733   3.169         NO
 4   61.7590   57.9091   -3.8499   -6.23   1.504   3.169         NO
 5  228.7590  228.8182     .0592     .03    .006   3.169         NO
 6  281.7590  266.9167  -14.8423   -5.27   1.134   3.106         NO
 7  551.7590  533.1667  -18.5924   -3.37    .626   3.106         NO
 8  600.7590  624.1667   23.4076    3.90    .710   3.106         NO
 9  799.7590  821.5833   21.8243    2.73   1.161   3.106         NO
10  858.7590  912.4167   53.6576    6.25   1.650   3.106         NO
------------------------------------------------------------------------
```

```
File Name:  as-9
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***   Single Operator Precision    ***
----------------------------------------
Analyte:  As          Matrix:  Estuarine
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):     3.8937
          Slope (b):      .0858
    =============================
                                           Single
           Sample Weights                Operator   Estimated
    Pair   Size       (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      11     95.68      5.4590      4.5515      4.3619
      2      10      3.97     56.0590      3.9836      8.7012
      3      11       .26    255.2590     19.2361     25.7840
      4      12       .06    576.2590     88.2279     53.3121
      5      12       .03    829.2590     83.3995     75.0087
    -----------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    =========================================================
      a:     4.8596      Intercept (a'):     1.5810
      b:     1.0040          Slope (b'):      .0040
    =========================================================
                                                  Single
           Sample Weight                Operator   Estimated
    Pair   Size      (%)        Conc     Std Dev     Std Dev
    ---------------------------------------------------------
      1      11    19.60      5.4590      4.5515      4.9672
      2      10    17.60      5.4590      3.9836      6.0847
      3      11    19.60     50.3590     19.2361     13.5267
      4      12    21.60     61.7590     88.2279     49.0099
      5      12    21.60    228.7590     83.3995    135.1886
    ---------------------------------------------------------
```

```
File Name:  as-9
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***       Overall Precision        ***
----------------------------------------
Analyte:  As          Matrix:  Estuarine
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Overall Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):     4.7807
          Slope (b):      .1365
    =============================
    Conc   Sample   Weights                 Overall   Estimated
    Level  Size         (%)        Conc     Std Dev     Std Dev
    -------------------------------------------------------------
      1      11       34.83      5.4590      6.2715      5.5259
      2      11       34.83      5.4590      7.2858      5.5259
      3      11       13.57     50.3590      7.6967     11.6558
      4      11       11.31     61.7590      8.7060     13.2122
      5      11        2.18    228.7590     35.4893     36.0116
      6      12        1.73    281.7590     46.3644     43.2473
      7      12         .55    551.7590    105.2130     80.1086
      8      12         .48    600.7590    116.8572     86.7982
      9      12         .28    799.7590     66.6121    113.9663
     10      12         .25    858.7590    115.2693    122.0212
    -------------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    ===========================================================
      a:     9.2703      Intercept (a'):     2.2268
      b:     1.0034          Slope (b'):      .0034
    ===========================================================
    Conc   Sample   Weight                 Overall   Estimated
    Level  Size        (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      11       9.51      5.4590      6.2715      9.4422
      2      11       9.51      5.4590      7.2858      9.4422
      3      11       9.51     50.3590      7.6967     10.9827
      4      11       9.51     61.7590      8.7060     11.4123
      5      11       9.51    228.7590     35.4893     20.0217
      6      12      10.49    281.7590     46.3644     23.9319
      7      12      10.49    551.7590    105.2130     59.3841
      8      12      10.49    600.7590    116.8572     70.0325
      9      12      10.49    799.7590     66.6121    136.8368
     10      12      10.49    858.7590    115.2693    166.8979
    -----------------------------------------------------------
```

```
File Name:  as-9
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ************  Recovery  **************
----------------------------------------
Analyte:  As          Matrix:  Estuarine
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Recovery ***

    - Linear Model - X = b*T + a
    =============================
      Intercept (a):     -.7400
          Slope (b):     1.0034
    =============================
    Conc   Sample   Weights                 Mean   Estimated
    Level  Size         (%)      Conc      Result      Result
    ----------------------------------------------------------
      1      11     40.73      5.4590      4.1909      4.7378
      2      11     40.73      5.4590      6.7273      4.7378
      3      11      9.15     50.3590     46.4364     49.7922
      4      11      7.12     61.7590     57.9091     61.2314
      5      11       .96    228.7590    228.8182    228.8058
      6      12       .73    281.7590    266.9167    281.9881
      7      12       .21    551.7590    533.1667    552.9168
      8      12       .18    600.7590    624.1667    602.0853
      9      12       .10    799.7590    821.5833    801.7698
     10      12       .09    858.7590    912.4167    860.9727
    ----------------------------------------------------------
```

```
File Name:  as-9
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***     Precision vs Recovery      ***
----------------------------------------
Analyte:  As          Matrix:  Estuarine
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision vs Recovery ***
           (Obtained by Substitution)

     - Linear Model - s = f*X + e
    ==============================
        Intercept (e):     4.6312
            Slope (f):      .0855
    ==============================


     - Curvilinear Model - s = e*(f**X)
    ====================================
        Intercept (e):     4.8740
                  (f):     1.0040
    ====================================



 *** Overall Precision vs Recovery ***
      (Obtained by Substitution)

     - Linear Model - s = f*X + e
     =============================
        Intercept (e):     5.5181
            Slope (f):      .1361
     =============================


     - Curvilinear Model - s = e*(f**X)
     ===================================
        Intercept (e):     9.2933
                  (f):     1.0034
     ===================================
```

```
as-10.dat

As    10   1     3.9000    5.7000   65.7000   98.2000  316.0000  387.0000  660.0000  684.0000  510.0000  670.0000
As    10   2    -0.5000   -1.1000   58.0000   66.0000  300.0000   37.7000  712.0000  816.0000  993.0000 1089.0000
As    10   5    12.0000   19.0000   82.0000  108.0000  341.0000  424.0000  731.0000  802.0000  917.0000  984.0000
As    10   6     5.0000    5.0000   81.0000  119.0000  367.0000  481.0000  811.0000  879.0000  965.0000 1026.0000
As    10   7    -4.4200    5.4800   57.0000   83.0000  321.0000  403.0000  697.0000  772.0000  841.0000  938.0000
As    10   8     0.0000    0.0000   18.3000   20.7000   45.4000   40.8000  836.0000  944.0000  928.0000  992.0000
As    10  10    36.0000    6.0000   45.0000   58.0000  217.0000  474.0000  739.0000  668.0000  790.0000  917.0000
As    10  15     4.7000    3.0000   62.0000   81.0000  288.0000  348.0000  736.0000  595.0000  775.0000  931.0000
As    10  16    52.2000    9.0000  175.0000  122.0000  422.0000  589.0000  800.0000  770.0000  988.0000  112.0000
As    10  17     6.0000   57.0000  100.0000  140.0000  400.0000  490.0000  220.0000  930.0000 1080.0000  770.0000
As    10  20    13.0000   18.0000   94.0000  118.0000  364.0000  448.0000  779.0000  855.0000  952.0000 1062.0000
As    10  21    37.0000   37.9000   59.0000   87.0000  310.0000  389.0000  633.0000  675.0000  765.0000  819.0000
As    10  24    21.4000   21.5000   96.6000  158.0000  375.0000  680.0000  779.0000  950.0000 1090.0000 1156.0000
As    10  25     0.0000    0.0000   52.8000  294.0000  380.0000  384.0000  648.0000  713.0000  818.0000  889.0000
As    10  26    -1.0000   -1.0000   64.0000   84.0000  323.0000  394.0000  725.0000  737.0000  904.0000  973.0000
As    10  27   -20.0000  -10.0000   60.0000   90.0000  350.0000  430.0000  670.0000  810.0000  840.0000  960.0000
```

```
File Name:  as-10
Data Validation File (.DA~)

******************************************************************************
***                   Parameter and Data Validation File                   ***
******************************************************************************
   Analyte:  As              Matrix:  Acid Mine Drainage
   Project:  AMQ-TC       Matrix ID:  10
      Date:  12/13/1995      Method:  GFAAS
     Pairs:  5
     Units:  ug/L

--------------------------------------------------------------------------------------------------------------------------------
Level          1          2            3          4            5          6            7          8            9         10
--------------------------------------------------------------------------------------------------------------------------------
Spike         8.3055      .0000      63.8000    30.4000     229.0000    82.0000     288.0000    70.0000     101.0000    70.0000
Spike
Increment      .0000      .0000      63.8000    94.2000     323.2000   405.2000     693.2000   763.2000     864.2000   934.2000
--------------------------------------------------------------------------------------------------------------------------------

                 Final Concentration
         -----------------------------------------------------------------------------------------------------------------------
Lab ID        8.3055     8.3055      72.1055   102.5055     331.5055   413.5055     701.5055   771.5055     872.5055   942.5055
--------------------------------------------------------------------------------------------------------------------------------
    1         3.9000     5.7000      65.7000    98.2000     316.0000   387.0000     660.0000   684.0000  o  510.0000   670.0000
    2         -.5000    -1.1000      58.0000    66.0000     300.0000    37.7000     712.0000   816.0000     993.0000  1089.0000
    5        12.0000    19.0000      82.0000   108.0000     341.0000   424.0000     731.0000   802.0000     917.0000   984.0000
    6         5.0000     5.0000      81.0000   119.0000     367.0000   481.0000     811.0000   879.0000     965.0000  1026.0000
    7        -4.4200     5.4800      57.0000    83.0000     321.0000   403.0000     697.0000   772.0000     841.0000   938.0000
    8          .0000      .0000      18.3000    20.7000  o   45.4000    40.8000     836.0000   944.0000     928.0000   992.0000
   10        36.0000     6.0000      45.0000    58.0000     217.0000   474.0000     739.0000   668.0000     790.0000   917.0000
   15         4.7000     3.0000      62.0000    81.0000     288.0000   348.0000     736.0000   595.0000     775.0000   931.0000
   16        52.2000     9.0000  o  175.0000   122.0000     422.0000   589.0000     800.0000   770.0000     988.0000o  112.0000
   17         6.0000o   57.0000     100.0000   140.0000     400.0000   490.0000  o  220.0000   930.0000    1080.0000   770.0000
   20        13.0000    18.0000      94.0000   118.0000     364.0000   448.0000     779.0000   855.0000     952.0000  1062.0000
   21        37.0000?   37.9000      59.0000    87.0000     310.0000   389.0000     633.0000   675.0000     765.0000   819.0000
   24    r   21.4000r   21.5000  r   96.6000r  158.0000  r  375.0000r  680.0000  r  779.0000r  950.0000  r 1090.0000r 1156.0000
   25          .0000      .0000      52.8000o  294.0000     380.0000   384.0000     648.0000   713.0000     818.0000   889.0000
   26        -1.0000    -1.0000      64.0000    84.0000     323.0000   394.0000     725.0000   737.0000     904.0000   973.0000
   27       -20.0000   -10.0000      60.0000    90.0000     350.0000   430.0000     670.0000   810.0000     840.0000   960.0000
--------------------------------------------------------------------------------------------------------------------------------
```

```
as-5.daf

As    10   1     3.9000    5.7000   65.7000   98.2000  316.0000  387.0000  660.0000  684.0000o           670.0000
As    10   2     -.5000   -1.1000   58.0000   66.0000  300.0000   37.7000  712.0000  816.0000  993.0000 1089.0000
As    10   5    12.0000   19.0000   82.0000  108.0000  341.0000  424.0000  731.0000  802.0000  917.0000  984.0000
As    10   6     5.0000    5.0000   81.0000  119.0000  367.0000  481.0000  811.0000  879.0000  965.0000 1026.0000
As    10   7    -4.4200    5.4800   57.0000   83.0000  321.0000  403.0000  697.0000  772.0000  841.0000  938.0000
As    10   8      .0000     .0000   18.3000   20.7000o            40.8000  836.0000  944.0000  928.0000  992.0000
As    10  10    36.0000    6.0000   45.0000   58.0000  217.0000  474.0000  739.0000  668.0000  790.0000  917.0000
As    10  15     4.7000    3.0000   62.0000   81.0000  288.0000  348.0000  736.0000  595.0000  775.0000  931.0000
As    10  16    52.2000    9.0000o            122.0000  422.0000  589.0000  800.0000  770.0000  988.0000o
As    10  17     6.0000o            100.0000  140.0000  400.0000  490.0000o            930.0000 1080.0000  770.0000
As    10  20    13.0000   18.0000   94.0000  118.0000  364.0000  448.0000  779.0000  855.0000  952.0000 1062.0000
As    10  21    37.0000   37.9000   59.0000   87.0000  310.0000  389.0000  633.0000  675.0000  765.0000  819.0000
As    10  25      .0000     .0000   52.8000o            380.0000  384.0000  648.0000  713.0000  818.0000  889.0000
As    10  26    -1.0000   -1.0000   64.0000   84.0000  323.0000  394.0000  725.0000  737.0000  904.0000  973.0000
As    10  27   -20.0000  -10.0000   60.0000   90.0000  350.0000  430.0000  670.0000  810.0000  840.0000  960.0000
```

```
File Name:  as-10
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Acid Mine Drainage
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------------------------
 ***        Results of 5x - 1/5x Mean Error Check        ***
 ***         Questionable Data (Positive Values)         ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean
 Lev   No   No     Result     Result                   Ratio
-------------------------------------------------------------
  4      8  1    107.9313    20.7000                    .19
  5      8  1    319.9625    45.4000                    .14
  6      2  1    399.9688    37.7000                    .09
  6      8  1    399.9688    40.8000                    .10
 10     16  1    893.0000   112.0000                    .13
-------------------------------------------------------------
Total Number of Questionable Observations:     5


-------------------------------------------------------------
 ***        Results of Factor of 5 Error Check           ***
 ***          Questionable Data (All Values)             ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean                Mean    Obs
 Lev   No   No     Result     Result     Dev     Dev   Ratio
-------------------------------------------------------------
  7    17   1    698.5000   220.0000   82.875  478.500  5.77
 10    16   1    893.0000   112.0000  150.625  781.000  5.19
-------------------------------------------------------------
Total Number of Questionable Observations:     2


File Name:  as-10
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Acid Mine Drainage
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
----------------------------------------------
 ***      Laboratory Ranking Results      ***
 ***   Two-Tailed 5% Significance Level   ***
 ***--------------------------------------***
 ***     Upper Critical Value:    127.0   ***
 ***     Lower Critical Value:     42.0   ***
----------------------------------------------

      Ranks
     ----------------------------------------------------------------------------
       Rank  Level  Level  Level  Level  Level  Level  Level  Level  Level  Level
Lab    Sums    1      2      3      4      5      6      7      8      9     10
---- ----------------------------------------------------------------------------
  1    57.0   7.00   9.00  10.00   9.00   6.00   5.00   4.00   4.00   1.00   2.00
  2    66.0   4.00   2.00   5.00   3.00   4.00   1.00   7.00  11.00  14.00  15.00
  5   102.0  11.00  13.00  12.00  10.00   9.00   9.00   9.00   9.00   9.00  11.00
  6   117.0   9.00   7.00  11.00  12.00  12.00  13.00  15.00  13.00  12.00  13.00
  7    63.0   2.00   8.00   4.00   5.00   7.00   8.00   6.00   8.00   7.00   8.00
  8    68.0   5.50   4.50   1.00   1.00   1.00   2.00  16.00  15.00  10.00  12.00
 10    65.0  14.00  10.00   2.00   2.00   2.00  12.00  11.00   2.00   4.00   6.00
 15    53.0   8.00   6.00   8.00   4.00   3.00   3.00  10.00   1.00   3.00   7.00
 16   122.0  16.00  11.00  16.00  13.00  16.00  15.00  14.00   7.00  13.00   1.00
 17   117.0  10.00  16.00  15.00  14.00  15.00  14.00   1.00  14.00  15.00   3.00
 20   119.5  12.00  12.00  13.00  11.00  11.00  11.00  12.50  12.00  11.00  14.00
 21    65.0  15.00  15.00   6.00   7.00   5.00   6.00   2.00   3.00   2.00   4.00
 24   145.5  13.00  14.00  14.00  15.00  13.00  16.00  12.50  16.00  16.00  16.00
 25    65.0   5.50   4.50   3.00  16.00  14.00   4.00   3.00   5.00   5.00   5.00
 26    68.0   3.00   3.00   9.00   6.00   8.00   7.00   8.00   6.00   8.00  10.00
 27    67.0   1.00   1.00   7.00   8.00  10.00  10.00   5.00  10.00   6.00   9.00
-------------------------------------------------
 *** Laboratory  24 Rejected; Rank Sum  145.5 ***
-------------------------------------------------

File Name:  as-10
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Acid Mine Drainage
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------
 ***    Outlier Testing Results      ***
 *** Two-Sided 5% Significance Level ***
-----------------------------------------

--------------------
   - Outlier(s) -
--------------------
 Lev  Iter  Lab  Rep     Result       Mean    Std Dev    t     Crit t   n
----------------------------------------------------------------------------
  2     1    17   1     57.0000    10.2653    17.1245   2.729   2.549   15
  3     1    16   1    175.0000    71.5867    34.8204   2.970   2.549   15
  4     1    25   1    294.0000   104.5933    60.0828   3.152   2.549   15
  5     1     8   1     45.4000   316.2933    89.9398   3.012   2.549   15
  7     1    17   1    220.0000   693.1334   144.1724   3.282   2.549   15
  9     1     1   1    510.0000   871.0667   135.2534   2.670   2.549   15
  *     1    16   1    112.0000   875.4667   238.0549   3.207   2.549   15
----------------------------------------------------------------------------
```

```
File Name:  as-10
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Acid Mine Drainage
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------
 *** Results of Normality Testing ***
-------------------------------------------

-------------------------
   - Normality Tests -
-------------------------
               Test  Normality      Test          Critical
   Level  n    Type  Accept/Reject  Statistic     Value(s)
---------------------------------------------------------------
     1    15     W            R        .8684      .881   ---
     2    14     W            R        .8646      .874   ---
     3    14     W     A               .9406      .874   ---
     4    14     W     A               .9601      .874   ---
     5    14     W     A               .9699      .874   ---
     6    15     W            R        .7727      .881   ---
     7    14     W     A               .9622      .874   ---
     8    15     W     A               .9778      .881   ---
     9    14     W     A               .9551      .874   ---
    10    14     W     A               .9393      .874   ---
-------------------------------
 - 3 Normality Rejection(s) -
-------------------------------
```

```
File Name:  as-10
Data Preparation File (.PRP)


Analyte:  As     Matrix:  Acid Mine Drainage
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------------
 ***         Data Removal Tracking         ***
 *** Simple Count of Remaining Data Points ***
 ***          After Removal Tests          ***
-----------------------------------------------

             Points   After Lab Ranking  After Outlier Testing
               As     -----------------  ---------------------
 Lev  Mtrx  Received     Points    %         Points       %

 ---  ----  --------  ---------  ------  ----------     ------
  1    10       16          15    93.8          15       93.8
  2    10       16          15    93.8          14       87.5
  3    10       16          15    93.8          14       87.5
  4    10       16          15    93.8          14       87.5
  5    10       16          15    93.8          14       87.5
  6    10       16          15    93.8          15       93.8
  7    10       16          15    93.8          14       87.5
  8    10       16          15    93.8          15       93.8
  9    10       16          15    93.8          14       87.5
 10    10       16          15    93.8          14       87.5
 ---  ----  --------  ---------  ------  ----------     ------
Totals:        160         150    93.8         143       89.4
--------------------------------------------------------------
```

```
File Name:  as-10
Statistical Analysis File (.STT)


----------------------------------------
 *** Summary Performance Statistics ***
----------------------------------------
Analyte:  As          Matrix:  Acid Mine Drainage
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

------------------------------------------------------------------------------------------------------------------------
            LEVEL:         1         2         3         4         5         6         7         8         9        10
------------------------------------------------------------------------------------------------------------------------
YOUDEN PAIRS:         Pair 1    Pair 1    Pair 2    Pair 2    Pair 3    Pair 3    Pair 4    Pair 4    Pair 5    Pair 5
                       (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)
------------------------------------------------------------------------------------------------------------------------
CONCENTRATION:        8.3055    8.3055   72.1055  102.5055  331.5055  413.5055  701.5055  771.5055  872.5055  942.5055
------------------------------------------------------------------------------------------------------------------------
RECOVERY:
 Observations             15        14        14        14        14        15        14        15        14        14
 Mean Result          9.5920    6.9271   64.2000   91.0643  335.6429  381.3000  726.9286  776.6667  896.8571  930.0000
 Bias                 1.2865   -1.3784   -7.9055  -11.4412    4.1374  -32.2055   25.4231    5.1612   24.3517  -12.5055
 Relative Bias %     15.4897  -16.5957  -10.9638  -11.1616    1.2481   -7.7884    3.6241     .6690    2.7910   -1.3268
 Maximum Result      52.2000   37.9000  100.0000  140.0000  422.0000  589.0000  836.0000  944.0000 1080.0000 1089.0000
 Minimum Result     -20.0000  -10.0000   18.3000   20.7000  217.0000   37.7000  633.0000  595.0000  765.0000  670.0000
------------------------------------------------------------------------------------------------------------------------
SINGLE OPERATOR PRECISION:   Pair 1              Pair 2              Pair 3              Pair 4              Pair 5
   Observations                  14                  13                  14                  14                  13
   Standard Deviation       10.6085              7.8177             79.0047             53.5711             81.5664
   Correction Factor         1.0194              1.0210              1.0194              1.0194              1.0210
   Corrected Std Dev        10.8143              7.9821             80.5372             54.6102             83.2815
   Relative Std Dev (%)    130.2064             10.2820             22.4176              7.2557              9.1175
------------------------------------------------------------------------------------------------------------------------
OVERALL PRECISION:
 Observations              15        14        14        14        14        15        14        15        14        14
 Standard Deviation   18.5969   11.6531   20.5992   30.5109   51.6074  150.7063   62.7295  100.3022   94.6360  113.9723
 Correction Factor     1.0180    1.0194    1.0194    1.0194    1.0194    1.0180    1.0194    1.0180    1.0194    1.0194
 Corrected Std Dev    18.9317   11.8792   20.9988   31.1027   52.6085  153.4194   63.9463  102.1078   96.4717  116.1831
 Relative Std Dev %  197.3696  171.4876   32.7084   34.1547   15.6739   40.2359    8.7968   13.1469   10.7566   12.4928
------------------------------------------------------------------------------------------------------------------------
```

```
File Name:  as-10
Statistical Analysis File (.STT)


----------------------------------
  *** Results of Bias Testing ***
----------------------------------
 Analyte:  As          Matrix:  Acid Mine Drainage
 Project:  AMQ-TC      Method:  GFAAS
    Date:  12/13/1995
   Units:  ug/L

-------------------------------------------------------------------------
                                    Rel.    Obs     Crit   Statistically
Conc.             Mean              Bias      t        t     Significant
Level   Conc     Result      Bias    (%)    Value    Value   (1% Two-Tail)
-------------------------------------------------------------------------
 1    8.3055    9.5920    1.2865   15.49    .268    2.977         NO
 2    8.3055    6.9271   -1.3784  -16.60    .443    3.012         NO
 3   72.1055   64.2000   -7.9055  -10.96   1.436    3.012         NO
 4  102.5055   91.0643  -11.4412  -11.16   1.403    3.012         NO
 5  331.5055  335.6429    4.1374    1.25    .300    3.012         NO
 6  413.5055  381.3000  -32.2055   -7.79    .828    2.977         NO
 7  701.5055  726.9286   25.4231    3.62   1.516    3.012         NO
 8  771.5055  776.6667    5.1612     .67    .199    2.977         NO
 9  872.5055  896.8571   24.3517    2.79    .963    3.012         NO
10  942.5055  930.0000  -12.5055   -1.33    .411    3.012         NO
-------------------------------------------------------------------------
```

```
File Name:  as-10
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***   Single Operator Precision    ***
----------------------------------------
Analyte:  As          Matrix:  Acid Mine Drainage
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):     8.6122
          Slope (b):      .0977
    =============================
                                           Single
           Sample Weights                Operator   Estimated
    Pair   Size       (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      14     57.04      8.3055     10.8143      9.4237
      2      13     29.05     87.3055      7.9821     17.1421
      3      14      8.49    372.5055     80.5372     45.0068
      4      14      3.26    736.5055     54.6102     80.5703
      5      13      2.16    907.5055     83.2815     97.2774
    -----------------------------------------------------------



    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    =========================================================
      a:    11.5809      Intercept (a'):     2.4494
      b:     1.0024          Slope (b'):      .0024
    =========================================================
                                                  Single
           Sample Weight                Operator   Estimated
    Pair   Size      (%)        Conc     Std Dev     Std Dev
    ---------------------------------------------------------
      1      14    20.65      8.3055     10.8143     11.8148
      2      13    19.03      8.3055      7.9821     14.2896
      3      14    20.65     72.1055     80.5372     28.3919
      4      14    20.65    102.5055     54.6102     68.1950
      5      13    19.03    331.5055     83.2815    102.9276
    ---------------------------------------------------------
```

```
File Name:  as-10
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***       Overall Precision        ***
----------------------------------------
Analyte:  As          Matrix:  Acid Mine Drainage
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Overall Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):    16.6175
          Slope (b):      .1264
    =============================
    Conc   Sample   Weights                 Overall   Estimated
    Level  Size        (%)        Conc     Std Dev     Std Dev
    -------------------------------------------------------------
      1      15       27.17      8.3055     18.9317     17.6675
      2      14       25.20      8.3055     11.8792     17.6675
      3      14       16.70     72.1055     20.9988     25.7334
      4      14       14.10    102.5055     31.1027     29.5768
      5      14        5.42    331.5055     52.6085     58.5282
      6      15        4.53    413.5055    153.4194     68.8951
      7      14        2.08    701.5055     63.9463    105.3056
      8      15        1.95    771.5055    102.1078    114.1554
      9      14        1.51    872.5055     96.4717    126.9243
     10      14        1.34    942.5055    116.1831    135.7741
    -------------------------------------------------------------



    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    ===========================================================
      a:    21.4233      Intercept (a'):     3.0645
      b:     1.0020          Slope (b'):      .0020
    ===========================================================
    Conc   Sample   Weight                 Overall   Estimated
    Level  Size       (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      15      10.54      8.3055     18.9317     21.7817
      2      14       9.77      8.3055     11.8792     21.7817
      3      14       9.77     72.1055     20.9988     24.7419
      4      14       9.77    102.5055     31.1027     26.2908
      5      14       9.77    331.5055     52.6085     41.5378
      6      15      10.54    413.5055    153.4194     48.9297
      7      14       9.77    701.5055     63.9463     86.9744
      8      15      10.54    771.5055    102.1078    100.0257
      9      14       9.77    872.5055     96.4717    122.3831
     10      14       9.77    942.5055    116.1831    140.7478
    -----------------------------------------------------------
```

```
File Name:  as-10
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ************  Recovery  **************
----------------------------------------
Analyte:  As          Matrix:  Acid Mine Drainage
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Recovery ***

    - Linear Model - X = b*T + a
    =============================
      Intercept (a):    -2.6439
          Slope (b):      .9988
    =============================
    Conc   Sample   Weights                  Mean   Estimated
    Level  Size         (%)      Conc      Result      Result
    ---------------------------------------------------------
      1      15     34.00      8.3055      9.5920      5.6517
      2      14     31.73      8.3055      6.9271      5.6517
      3      14     14.96     72.1055     64.2000     69.3759
      4      14     11.32    102.5055     91.0643     99.7397
      5      14      2.89    331.5055    335.6429    328.4675
      6      15      2.24    413.5055    381.3000    410.3700
      7      14       .89    701.5055    726.9286    698.0276
      8      15       .81    771.5055    776.6667    767.9445
      9      14       .61    872.5055    896.8571    868.8244
     10      14       .54    942.5055    930.0000    938.7411
    ---------------------------------------------------------
```

```
File Name:  as-10
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***     Precision vs Recovery      ***
----------------------------------------
Analyte:  As          Matrix:  Acid Mine Drainage
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision vs Recovery ***
           (Obtained by Substitution)

     - Linear Model - s = f*X + e
    ==============================
        Intercept (e):    11.2593
            Slope (f):      .0978
    ==============================


     - Curvilinear Model - s = e*(f**X)
    ====================================
        Intercept (e):    11.6549
                  (f):     1.0024
    ====================================



 *** Overall Precision vs Recovery ***
       (Obtained by Substitution)

     - Linear Model - s = f*X + e
     =============================
        Intercept (e):    19.2645
            Slope (f):      .1266
     =============================


     - Curvilinear Model - s = e*(f**X)
     ===================================
        Intercept (e):    21.5369
                  (f):     1.0020
     ===================================
```

```
cd-5.dat

Cd     5   1     0.0200   -0.0200    0.5700    1.0000    2.1800    3.0800    4.7100    5.8500    8.1100    9.7000
Cd     5   2     0.0000    0.0000    0.7000    1.3000    4.1000    3.9000    6.4000    7.8000    8.4000    9.6000
Cd     5   6    -0.1000   -0.1000    0.5000    1.1000    2.5000    3.3000    5.2000    6.7000    8.5000    9.7000
Cd     5   7    -0.0175   -0.0646    0.5020    0.9860    2.3000    3.2400    5.0900    6.4100    7.1000    8.8000
Cd     5   8     0.2000    0.1000    0.8000    1.6000    3.0000    3.9000    5.3000    6.4000    8.2000    9.4000
Cd     5  10     0.0000   -0.1000    0.4500    1.1000    2.2000    2.6000    4.8000    5.5000    7.2000    7.3000
Cd     5  11     0.0000    1.0000    0.7000    1.7000    2.4000    3.3000    4.6000    5.8000    8.5000    9.9000
Cd     5  15     0.1000    0.0000    0.6000    1.1000    2.2000    3.0000    4.9000    6.2000    9.0000   10.2000
Cd     5  16    -0.0010   -0.0010   -0.0010    1.1000    0.0000    1.1000    2.2000    3.3000    4.4000    5.5000
Cd     5  17     0.1000    0.0000    0.4000   26.7000    2.1000    3.5000   17.6000    6.5000    9.6000   18.6000
Cd     5  20     0.0000    0.0000    0.5000    1.1000    2.4000    3.2000    4.8000    6.1000    8.7000   10.0000
Cd     5  21     0.1000    0.1000    0.6000    1.1000    2.4000    3.2000    4.8000    6.1000    8.7000    9.5000
Cd     5  22    -0.0800   -0.1100    0.6200    1.0700    2.8000    3.4000    4.8000    6.0500    8.7000   10.0000
Cd     5  24     0.2500    0.2400    0.8100    1.3400    3.2200    3.6900    6.0900    6.2200    9.0800   10.8000
Cd     5  25     0.1000    0.1000    0.6000    1.1000    2.4000    3.1000    4.7000    6.5000    8.6000    9.9000
Cd     5  26    -0.2000   -0.2000    0.6000    1.3000    2.6000    3.4000    4.9000    6.5000    9.0000   11.0000
Cd     5  27     0.1000    0.1000    0.6000    1.1000    2.0000    2.7000    4.0000    4.2000    8.3000    9.3000
```

```
File Name:  cd-5
Data Validation File (.DA~)

******************************************************************************
***                   Parameter and Data Validation File                   ***
******************************************************************************
   Analyte:  Cd              Matrix:  Reagent Grade Water
   Project:  AMQ-TC       Matrix ID:   5
      Date:  12/13/1995      Method:  GFAAS
     Pairs:  5
     Units:  ug/L

---------------------------------------------------------------------------------------------------------------------------------
Level          1          2            3          4            5          6            7          8            9         10
---------------------------------------------------------------------------------------------------------------------------------
Spike          .0084      .0000        .5000      .6000       1.2000      .8000       1.6000     1.2000       2.4000     1.2000
Spike
Increment      .0000      .0000        .5000     1.1000       2.3000     3.1000       4.7000     5.9000       8.3000     9.5000
---------------------------------------------------------------------------------------------------------------------------------

                 Final Concentration
         ------------------------------------------------------------------------------------------------------------------------
Lab ID         .0084      .0084        .5084     1.1084       2.3084     3.1084       4.7084     5.9084       8.3084     9.5084
---------------------------------------------------------------------------------------------------------------------------------
    1          .0200     -.0200        .5700     1.0000       2.1800     3.0800       4.7100     5.8500       8.1100     9.7000
    2          .0000      .0000        .7000     1.3000  o    4.1000     3.9000  ?    6.4000?    7.8000       8.4000     9.6000
    6         -.1000     -.1000        .5000     1.1000       2.5000     3.3000       5.2000     6.7000       8.5000     9.7000
    7         -.0175     -.0646        .5020      .9860       2.3000     3.2400       5.0900     6.4100  o    7.1000     8.8000
    8          .2000      .1000        .8000     1.6000       3.0000     3.9000       5.3000     6.4000       8.2000     9.4000
   10    r     .0000r    -.1000  r     .4500r    1.1000  r    2.2000r    2.6000  r    4.8000r    5.5000  r    7.2000r    7.3000
   11          .0000o    1.0000        .7000     1.7000       2.4000     3.3000       4.6000     5.8000       8.5000     9.9000
   15          .1000      .0000        .6000     1.1000       2.2000     3.0000       4.9000     6.2000       9.0000    10.2000
   16    r    -.0010r    -.0010  r    -.0010r    1.1000  r     .0000r    1.1000  r    2.2000r    3.3000  r    4.4000r    5.5000
   17          .1000      .0000        .4000o   26.7000       2.1000     3.5000  o   17.6000     6.5000       9.6000o   18.6000
   20          .0000      .0000        .5000     1.1000       2.4000     3.2000       4.8000     6.1000       8.7000    10.0000
   21          .1000      .1000        .6000     1.1000       2.4000     3.2000       4.8000     6.1000       8.7000     9.5000
   22         -.0800     -.1100        .6200     1.0700       2.8000     3.4000       4.8000     6.0500       8.7000    10.0000
   24    r     .2500r     .2400  r     .8100r    1.3400  r    3.2200r    3.6900  r    6.0900r    6.2200  r    9.0800r   10.8000
   25          .1000      .1000        .6000     1.1000       2.4000     3.1000       4.7000     6.5000       8.6000     9.9000
   26         -.2000     -.2000        .6000     1.3000       2.6000     3.4000       4.9000     6.5000       9.0000    11.0000
   27          .1000      .1000        .6000     1.1000       2.0000     2.7000       4.0000o    4.2000       8.3000     9.3000
---------------------------------------------------------------------------------------------------------------------------------
```

```
cd-5.daf

Cd     5   1      .0200    -.0200     .5700    1.0000    2.1800    3.0800    4.7100    5.8500    8.1100    9.7000
Cd     5   2      .0000     .0000     .7000    1.3000o             3.9000    6.4000    7.8000    8.4000    9.6000
Cd     5   6     -.1000    -.1000     .5000    1.1000    2.5000    3.3000    5.2000    6.7000    8.5000    9.7000
Cd     5   7     -.0175    -.0646     .5020     .9860    2.3000    3.2400    5.0900    6.4100o             8.8000
Cd     5   8      .2000     .1000     .8000    1.6000    3.0000    3.9000    5.3000    6.4000    8.2000    9.4000
Cd     5  11      .0000o              .7000    1.7000    2.4000    3.3000    4.6000    5.8000    8.5000    9.9000
Cd     5  15      .1000     .0000     .6000    1.1000    2.2000    3.0000    4.9000    6.2000    9.0000   10.2000
Cd     5  17      .1000     .0000     .4000o             2.1000    3.5000o             6.5000    9.6000o
Cd     5  20      .0000     .0000     .5000    1.1000    2.4000    3.2000    4.8000    6.1000    8.7000   10.0000
Cd     5  21      .1000     .1000     .6000    1.1000    2.4000    3.2000    4.8000    6.1000    8.7000    9.5000
Cd     5  22     -.0800    -.1100     .6200    1.0700    2.8000    3.4000    4.8000    6.0500    8.7000   10.0000
Cd     5  25      .1000     .1000     .6000    1.1000    2.4000    3.1000    4.7000    6.5000    8.6000    9.9000
Cd     5  26     -.2000    -.2000     .6000    1.3000    2.6000    3.4000    4.9000    6.5000    9.0000   11.0000
Cd     5  27      .1000     .1000     .6000    1.1000    2.0000    2.7000    4.0000o             8.3000    9.3000
```

```
File Name:  cd-5
Data Preparation File (.PRP)

Analyte:  Cd     Matrix:  Reagent Grade Water
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------------------------
 ***       Results of 5x - 1/5x Mean Error Check        ***
 ***        Questionable Data (Positive Values)         ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean
 Lev   No   No     Result     Result                  Ratio
-------------------------------------------------------------
  2     11  1       .0965     1.0000                 10.37
  4     17  1      2.6939    26.7000                  9.91
-------------------------------------------------------------
Total Number of Questionable Observations:     2


-------------------------------------------------------------
 ***       Results of Factor of 5 Error Check           ***
 ***         Questionable Data (All Values)             ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean                  Mean    Obs
 Lev   No   No     Result     Result     Dev     Dev   Ratio
-------------------------------------------------------------
  2    11   1       .0614     1.0000     .150     .939  6.27
  4    17   1      2.6939    26.7000    2.824   24.006  8.50
  5    16   1      2.4000      .0000     .449    2.400  5.34
  6    16   1      3.1535     1.1000     .393    2.054  5.22
  7    17   1      5.5818    17.6000    1.570   12.018  7.66
  9    16   1      8.2406     4.4000     .729    3.841  5.27
 10    17   1      9.9529    18.6000    1.280    8.647  6.75
-------------------------------------------------------------
Total Number of Questionable Observations:     7
```

```
File Name:  cd-5
Data Preparation File (.PRP)

Analyte:  Cd     Matrix:  Reagent Grade Water
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
----------------------------------------------
 ***      Laboratory Ranking Results      ***
 ***   Two-Tailed 5% Significance Level   ***
 ***--------------------------------------***
 ***     Upper Critical Value:    135.0   ***
 ***     Lower Critical Value:     45.0   ***
----------------------------------------------

      Ranks
     ------------------------------------------------------------------------------
       Rank  Level  Level  Level  Level  Level  Level  Level  Level  Level  Level
Lab    Sums    1      2      3      4      5      6      7      8      9     10
---- ------------------------------------------------------------------------------
  1    56.5  10.00   6.00   7.00   2.00   4.00   5.00   5.00   5.00   4.00   8.50
  2   124.5   7.50   9.50  14.50  12.50  17.00  16.50  16.00  17.00   7.00   7.00
  6    86.0   2.00   3.50   4.50   7.50  12.00  10.50  13.00  16.00   8.50   8.50
  7    61.0   4.00   5.00   6.00   1.00   7.00   9.00  12.00  12.00   2.00   3.00
  8   127.0  16.00  13.50  16.00  15.00  15.00  16.50  14.00  11.00   5.00   5.00
 10    44.5   7.50   3.50   3.00   7.50   5.50   2.00   7.50   3.00   3.00   2.00
 11   101.0   7.50  17.00  14.50  16.00   9.50  10.50   3.00   4.00   8.50  10.50
 15    97.5  13.00   9.50  10.00   7.50   5.50   4.00  10.50   9.00  14.50  14.00
 16    26.5   5.00   7.00   1.00   7.50   1.00   1.00   1.00   1.00   1.00   1.00
 17   123.5  13.00   9.50   2.00  17.00   3.00  14.00  17.00  14.00  17.00  17.00
 20    85.5   7.50   9.50   4.50   7.50   9.50   7.50   7.50   7.50  12.00  12.50
 21    94.0  13.00  13.50  10.00   7.50   9.50   7.50   7.50   7.50  12.00   6.00
 22    85.5   3.00   2.00  13.00   3.00  14.00  12.50   7.50   6.00  12.00  12.50
 24   151.0  17.00  16.00  17.00  14.00  16.00  15.00  15.00  10.00  16.00  15.00
 25    98.0  13.00  13.50  10.00   7.50   9.50   6.00   4.00  14.00  10.00  10.50
 26   105.0   1.00   1.00  10.00  12.50  13.00  12.50  10.50  14.00  14.50  16.00
 27    63.0  13.00  13.50  10.00   7.50   2.00   3.00   2.00   2.00   6.00   4.00
-------------------------------------------------
 *** Laboratory  10 Rejected; Rank Sum   44.5 ***
 *** Laboratory  16 Rejected; Rank Sum   26.5 ***
 *** Laboratory  24 Rejected; Rank Sum  151.0 ***
-------------------------------------------------
```

```
File Name:  cd-5
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Reagent Grade Water
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------
 ***    Outlier Testing Results      ***
 *** Two-Sided 5% Significance Level ***
-----------------------------------------

--------------------
   - Outlier(s) -
--------------------
 Lev  Iter  Lab  Rep     Result       Mean    Std Dev    t     Crit t   n
----------------------------------------------------------------------------
  2     1    11   1      1.0000      .0647      .2839   3.294   2.507   14
  4     1    17   1     26.7000     3.0183     6.8194   3.473   2.507   14
  5     1     2   1      4.1000     2.5271      .5249   2.996   2.507   14
  7     1    17   1     17.6000     5.8429     3.4237   3.434   2.507   14
  8     1    27   1      4.2000     6.2221      .7587   2.665   2.507   14
  9     1     7   1      7.1000     8.5293      .5602   2.551   2.507   14
  *     1    17   1     18.6000    10.4000     2.4125   3.399   2.507   14
----------------------------------------------------------------------------
```

```
File Name:  cd-5
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Reagent Grade Water
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------
 *** Results of Normality Testing ***
-------------------------------------------

-------------------------
   - Normality Tests -
-------------------------
               Test  Normality      Test          Critical
   Level  n    Type  Accept/Reject  Statistic     Value(s)
---------------------------------------------------------------
     1    14     W     A              .9382      .874   ---
     2    13     W     A              .9017      .866   ---
     3    14     W     A              .9449      .874   ---
     4    13     W            R       .7615      .866   ---
     5    13     W     A              .9466      .866   ---
     6    14     W     A              .9341      .874   ---
     7    13     W            R       .8405      .866   ---
     8    13     W            R       .8176      .866   ---
     9    13     W     A              .9230      .866   ---
    10    13     W     A              .9452      .866   ---
-------------------------------
 - 3 Normality Rejection(s) -
-------------------------------
```

```
File Name:  cd-5
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Reagent Grade Water
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------------
 ***         Data Removal Tracking         ***
 *** Simple Count of Remaining Data Points ***
 ***          After Removal Tests          ***
-----------------------------------------------

             Points   After Lab Ranking  After Outlier Testing
               As     -----------------  ---------------------
 Lev  Mtrx  Received     Points    %         Points       %

 ---  ----  --------  ---------  ------  ----------     ------
  1     5       17          14    82.4          14       82.4
  2     5       17          14    82.4          13       76.5
  3     5       17          14    82.4          14       82.4
  4     5       17          14    82.4          13       76.5
  5     5       17          14    82.4          13       76.5
  6     5       17          14    82.4          14       82.4
  7     5       17          14    82.4          13       76.5
  8     5       17          14    82.4          13       76.5
  9     5       17          14    82.4          13       76.5
 10     5       17          14    82.4          13       76.5
 ---  ----  --------  ---------  ------  ----------     ------
Totals:        170         140    82.4         133       78.2
--------------------------------------------------------------
```

```
File Name:  cd-5
Statistical Analysis File (.STT)


----------------------------------------
 *** Summary Performance Statistics ***
----------------------------------------
Analyte:  Cd          Matrix:  Reagent Grade Water
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

------------------------------------------------------------------------------------------------------------------------
            LEVEL:         1         2         3         4         5         6         7         8         9        10
------------------------------------------------------------------------------------------------------------------------
YOUDEN PAIRS:         Pair 1    Pair 1    Pair 2    Pair 2    Pair 3    Pair 3    Pair 4    Pair 4    Pair 5    Pair 5
                       (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)
------------------------------------------------------------------------------------------------------------------------
CONCENTRATION:         .0084     .0084     .5084    1.1084    2.3084    3.1084    4.7084    5.9084    8.3084    9.5084
------------------------------------------------------------------------------------------------------------------------
RECOVERY:
 Observations             14        13        14        13        13        14        13        13        13        13
 Mean Result           .0230    -.0073     .5923    1.1966    2.4062    3.3014    4.9385    6.3777    8.6392    9.7692
 Bias                  .0146    -.0157     .0839     .0882     .0978     .1930     .2301     .4693     .3308     .2608
 Relative Bias %    174.2347 -186.6300   16.4999    7.9588    4.2347    6.2099    4.8862    7.9428    3.9819    2.7432
 Maximum Result        .2000     .1000     .8000    1.7000    3.0000    3.9000    6.4000    7.8000    9.6000   11.0000
 Minimum Result      -.2000    -.2000     .4000     .9860    2.0000    2.7000    4.0000    5.8000    8.1100    8.8000
------------------------------------------------------------------------------------------------------------------------
SINGLE OPERATOR PRECISION:   Pair 1              Pair 2              Pair 3              Pair 4              Pair 5
   Observations                  13                  13                  13                  12                  12
   Standard Deviation         .0298               .1143               .1351               .1410               .2092
   Correction Factor         1.0210              1.0210              1.0210              1.0230              1.0230
   Corrected Std Dev          .0304               .1167               .1379               .1443               .2140
   Relative Std Dev (%)    360.6674             13.2104              4.8059              2.5496              2.3254
------------------------------------------------------------------------------------------------------------------------
OVERALL PRECISION:
 Observations              14        13        14        13        13        14        13        13        13        13
 Standard Deviation     .1037     .0940     .1000     .2222     .2766     .3213     .5418     .5065     .3958     .5202
 Correction Factor     1.0194    1.0210    1.0194    1.0210    1.0210    1.0194    1.0210    1.0210    1.0210    1.0210
 Corrected Std Dev      .1057     .0960     .1020     .2269     .2824     .3275     .5532     .5172     .4042     .5312
 Relative Std Dev %  458.7046 *********   17.2160   18.9606   11.7362    9.9206   11.2025    8.1090    4.6783    5.4371
------------------------------------------------------------------------------------------------------------------------
```

```
File Name:  cd-5
Statistical Analysis File (.STT)


----------------------------------
  *** Results of Bias Testing ***
----------------------------------
 Analyte:  Cd          Matrix:  Reagent Grade Water
 Project:  AMQ-TC      Method:  GFAAS
    Date:  12/13/1995
   Units:  ug/L

------------------------------------------------------------------------
                                    Rel.    Obs     Crit   Statistically
Conc.             Mean              Bias      t        t     Significant
Level   Conc    Result      Bias     (%)   Value   Value   (1% Two-Tail)
------------------------------------------------------------------------
 1     .0084     .0230     .0146  174.23    .529   3.012         NO
 2     .0084    -.0073    -.0157  ******    .601   3.055         NO
 3     .5084     .5923     .0839   16.50   3.138   3.012        YES
 4    1.1084    1.1966     .0882    7.96   1.431   3.055         NO
 5    2.3084    2.4062     .0978    4.23   1.274   3.055         NO
 6    3.1084    3.3014     .1930    6.21   2.248   3.012         NO
 7    4.7084    4.9385     .2301    4.89   1.531   3.055         NO
 8    5.9084    6.3777     .4693    7.94   3.341   3.055        YES
 9    8.3084    8.6392     .3308    3.98   3.013   3.055         NO
10    9.5084    9.7692     .2608    2.74   1.808   3.055         NO
------------------------------------------------------------------------
```

```
File Name:  cd-5
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***   Single Operator Precision    ***
----------------------------------------
Analyte:  Cd          Matrix:  Reagent Grade Water
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):      .0604
          Slope (b):      .0202
    =============================
                                        Single
           Sample Weights              Operator   Estimated
    Pair   Size       (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      13     42.10       .0084       .0304       .0606
      2      13     30.00       .8084       .1167       .0768
      3      13     15.98      2.7084       .1379       .1152
      4      12      7.80      5.3084       .1443       .1677
      5      12      4.13      8.9084       .2140       .2405
    -----------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    =========================================================
      a:      .0621      Intercept (a'):    -2.7784
      b:     1.1715          Slope (b'):      .1582
    =========================================================
                                               Single
           Sample Weight              Operator   Estimated
    Pair   Size      (%)        Conc     Std Dev     Std Dev
    ---------------------------------------------------------
      1      13    20.70       .0084       .0304       .0622
      2      13    20.70       .0084       .1167       .0706
      3      13    20.70       .5084       .1379       .0954
      4      12    18.95      1.1084       .1443       .1439
      5      12    18.95      2.3084       .2140       .2544
    ---------------------------------------------------------
```

```
File Name:  cd-5
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***       Overall Precision        ***
----------------------------------------
Analyte:  Cd          Matrix:  Reagent Grade Water
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Overall Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):      .1112
          Slope (b):      .0600
    =============================
    Conc   Sample   Weights                 Overall   Estimated
    Level  Size        (%)        Conc     Std Dev     Std Dev
    -------------------------------------------------------------
      1      14       23.85       .0084       .1057       .1117
      2      13       21.98       .0084       .0960       .1117
      3      14       17.99       .5084       .1020       .1417
      4      13       12.37      1.1084       .2269       .1777
      5      13        7.64      2.3084       .2824       .2497
      6      14        6.35      3.1084       .3275       .2977
      7      13        3.75      4.7084       .5532       .3938
      8      13        2.83      5.9084       .5172       .4658
      9      13        1.78      8.3084       .4042       .6099
     10      13        1.46      9.5084       .5312       .6819
    -------------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    ===========================================================
      a:      .1386      Intercept (a'):    -1.9761
      b:     1.1910          Slope (b'):      .1748
    ===========================================================
    Conc   Sample   Weight                 Overall   Estimated
    Level  Size       (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      14      10.58       .0084       .1057       .1388
      2      13       9.75       .0084       .0960       .1388
      3      14      10.58       .5084       .1020       .1515
      4      13       9.75      1.1084       .2269       .1682
      5      13       9.75      2.3084       .2824       .2075
      6      14      10.58      3.1084       .3275       .2387
      7      13       9.75      4.7084       .5532       .3157
      8      13       9.75      5.9084       .5172       .3893
      9      13       9.75      8.3084       .4042       .5923
     10      13       9.75      9.5084       .5312       .7305
    -----------------------------------------------------------
```

```
File Name:  cd-5
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ************  Recovery  **************
----------------------------------------
Analyte:  Cd          Matrix:  Reagent Grade Water
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Recovery ***

    - Linear Model - X = b*T + a
    =============================
      Intercept (a):      .0166
          Slope (b):     1.0477
    =============================
    Conc   Sample   Weights                  Mean   Estimated
    Level  Size         (%)      Conc      Result      Result
    ---------------------------------------------------------
      1      14     29.18       .0084       .0230       .0254
      2      13     27.10       .0084      -.0073       .0254
      3      14     18.13       .5084       .5923       .5493
      4      13     10.70      1.1084      1.1966      1.1779
      5      13      5.42      2.3084      2.4062      2.4351
      6      14      4.10      3.1084      3.3014      3.2733
      7      13      2.18      4.7084      4.9385      4.9496
      8      13      1.56      5.9084      6.3777      6.2068
      9      13       .91      8.3084      8.6392      8.7213
     10      13       .73      9.5084      9.7692      9.9786
    ---------------------------------------------------------


File Name:  cd-5
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***     Precision vs Recovery      ***
----------------------------------------
Analyte:  Cd          Matrix:  Reagent Grade Water
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision vs Recovery ***
           (Obtained by Substitution)

     - Linear Model - s = f*X + e
    ==============================
        Intercept (e):      .0446
            Slope (f):      .0193
    ==============================


     - Curvilinear Model - s = e*(f**X)
    ====================================
        Intercept (e):      .0620
                  (f):     1.1630
    ====================================



 *** Overall Precision vs Recovery ***
       (Obtained by Substitution)

     - Linear Model - s = f*X + e
     =============================
        Intercept (e):      .0953
            Slope (f):      .0573
     =============================


     - Curvilinear Model - s = e*(f**X)
     ===================================
        Intercept (e):      .1382
                  (f):     1.1816
     ===================================
```

```
cd8.dat

Cd     8   1     0.4200    0.3900    1.0300    2.1800    5.1900    5.5100    8.7400   11.5800   15.7400   18.1600
Cd     8   2     0.0000    0.0000    0.6000    1.4000    3.8000    5.2000    7.1000    8.8000    8.5000   11.6000
Cd     8   6     0.1000    0.3000    0.9000    2.2000    4.5000    5.9000    7.3000    9.4000   12.3000   11.3000
Cd     8   7    -0.2100   -0.1420   -0.0120    1.1300    2.8000    3.6400    5.3900    7.0700    7.8000    9.2000
Cd     8   8     0.3000   -0.1000    0.4000    1.1000    2.8000    3.5000    4.8000    6.0000    7.7000    8.0000
Cd     8  10    -0.1000   -0.1000    0.4000    1.5500    3.4000    3.7500    6.4000    7.8500    8.2500   11.6500
Cd     8  11     0.1000    0.1000    0.4000    1.1000    3.2000    3.8000    5.3000    7.4000    8.8000   10.2000
Cd     8  15     0.1000    0.1000    0.5000    1.2000    3.2000    4.0000    5.8000    6.2000    7.7000   10.5000
Cd     8  16    -0.0010   -0.0020   -0.0040   -0.0020   -0.0020    0.0000    1.7000    3.9000    5.0000    5.6000
Cd     8  17     2.1000    0.5000  127.0000    4.3000    5.4000    4.4000    5.7000    8.3000   11.1000   12.3000
Cd     8  20     0.0000    0.0000    0.6000    1.5000    3.9000    5.2000    7.4000    9.9000   12.1000   14.0000
Cd     8  21    -0.1000   -0.1500    0.3000    1.1000    3.2000    4.0000    5.8000    7.4000    9.1000   12.0000
Cd     8  22     0.0000    0.0800    0.5100    1.0900    3.2000    4.0000    5.3000    6.9500    8.4000   10.2000
Cd     8  24     0.2600    0.7800    0.6900    1.5100    4.0700    5.2200    7.3900    9.6600   10.0000   16.2000
Cd     8  25     0.1000    0.1000    0.5000    1.2000    3.5000    4.2000    5.1000    8.0000    8.8000    8.8000
Cd     8  26    -0.1000   -0.1000    0.4000    1.4000    3.7000    4.4000    6.0000    8.0000    9.0000   12.0000
Cd     8  27     0.3000    0.1000    0.5000    1.0000    2.7000    3.5000    4.9000    7.1000    8.8000   10.6000
```

```
File Name:  cd-8
Data Validation File (.DA~)

******************************************************************************
***                   Parameter and Data Validation File                   ***
******************************************************************************
   Analyte:  Cd              Matrix:  Freshwater
   Project:  AMQ-TC       Matrix ID:   8
      Date:  12/13/1995      Method:  GFAAS
     Pairs:  5
     Units:  ug/L

---------------------------------------------------------------------------------------------------------------------------------
Level          1          2            3          4            5          6            7          8            9         10
---------------------------------------------------------------------------------------------------------------------------------
Spike          .0436      .0000        .4000      .7000      1.9000      .8000       1.6000     1.6000       1.6000     1.7000
Spike
Increment      .0000      .0000        .4000     1.1000      3.0000      3.8000       5.4000     7.0000       8.6000    10.3000
---------------------------------------------------------------------------------------------------------------------------------

                 Final Concentration
         ------------------------------------------------------------------------------------------------------------------------
Lab ID         .0436      .0436        .4436     1.1436      3.0436      3.8436       5.4436     7.0436       8.6436    10.3436
---------------------------------------------------------------------------------------------------------------------------------
    1    r     .4200r     .3900  r    1.0300r    2.1800  r   5.1900r     5.5100  r    8.7400r   11.5800  r   15.7400r   18.1600
    2          .0000      .0000        .6000     1.4000      3.8000      5.2000       7.1000     8.8000       8.5000    11.6000
    6    !     .1000!     .3000  !     .9000?    2.2000  !   4.5000!     5.9000  !    7.3000!    9.4000  !   12.3000!   11.3000
    7    !    -.2100!    -.1420  !    -.0120!    1.1300  !   2.8000!     3.6400  !    5.3900!    7.0700  !    7.8000!    9.2000
    8    !     .3000!    -.1000  !     .4000!    1.1000  !   2.8000!     3.5000  !    4.8000!    6.0000  !    7.7000!    8.0000
   10         -.1000     -.1000        .4000     1.5500      3.4000      3.7500       6.4000     7.8500       8.2500    11.6500
   11          .1000      .1000        .4000     1.1000      3.2000      3.8000       5.3000     7.4000       8.8000    10.2000
   15          .1000      .1000        .5000     1.2000      3.2000      4.0000       5.8000     6.2000       7.7000    10.5000
   16    r    -.0010r    -.0020  r    -.0040r    -.0020  r   -.0020r      .0000  r    1.7000r    3.9000  r    5.0000r    5.6000
   17    o    2.1000!     .5000  o  127.0000o    4.3000  o   5.4000!     4.4000  !    5.7000!    8.3000  !   11.1000!   12.3000
   20          .0000      .0000        .6000     1.5000      3.9000      5.2000       7.4000     9.9000      12.1000    14.0000
   21         -.1000     -.1500        .3000     1.1000      3.2000      4.0000       5.8000     7.4000       9.1000    12.0000
   22          .0000      .0800        .5100     1.0900      3.2000      4.0000       5.3000     6.9500       8.4000    10.2000
   24    r     .2600r     .7800  r     .6900r    1.5100  r   4.0700r     5.2200  r    7.3900r    9.6600  r   10.0000r   16.2000
   25          .1000      .1000        .5000     1.2000      3.5000      4.2000       5.1000     8.0000       8.8000     8.8000
   26         -.1000     -.1000        .4000     1.4000      3.7000      4.4000       6.0000     8.0000       9.0000    12.0000
   27          .3000      .1000        .5000     1.0000      2.7000      3.5000       4.9000     7.1000       8.8000    10.6000
---------------------------------------------------------------------------------------------------------------------------------
```

```
cd-8.daf

Cd     8   2      .0000     .0000     .6000    1.4000    3.8000    5.2000    7.1000    8.8000    8.5000   11.6000
Cd     8   6      .1000     .3000     .9000    2.2000    4.5000    5.9000    7.3000    9.4000   12.3000   11.3000
Cd     8   7     -.2100    -.1420    -.0120    1.1300    2.8000    3.6400    5.3900    7.0700    7.8000    9.2000
Cd     8   8      .3000    -.1000     .4000    1.1000    2.8000    3.5000    4.8000    6.0000    7.7000    8.0000
Cd     8  10     -.1000    -.1000     .4000    1.5500    3.4000    3.7500    6.4000    7.8500    8.2500   11.6500
Cd     8  11      .1000     .1000     .4000    1.1000    3.2000    3.8000    5.3000    7.4000    8.8000   10.2000
Cd     8  15      .1000     .1000     .5000    1.2000    3.2000    4.0000    5.8000    6.2000    7.7000   10.5000
Cd     8  17 o              .5000o         o         o                        4.4000    5.7000    8.3000   11.1000   12.3000
Cd     8  20      .0000     .0000     .6000    1.5000    3.9000    5.2000    7.4000    9.9000   12.1000   14.0000
Cd     8  21     -.1000    -.1500     .3000    1.1000    3.2000    4.0000    5.8000    7.4000    9.1000   12.0000
Cd     8  22      .0000     .0800     .5100    1.0900    3.2000    4.0000    5.3000    6.9500    8.4000   10.2000
Cd     8  25      .1000     .1000     .5000    1.2000    3.5000    4.2000    5.1000    8.0000    8.8000    8.8000
Cd     8  26     -.1000    -.1000     .4000    1.4000    3.7000    4.4000    6.0000    8.0000    9.0000   12.0000
Cd     8  27      .3000     .1000     .5000    1.0000    2.7000    3.5000    4.9000    7.1000    8.8000   10.6000
```

```
File Name:  cd-8
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Freshwater
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------------------------
 ***        Results of 5x - 1/5x Mean Error Check        ***
 ***         Questionable Data (Positive Values)         ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean
 Lev   No   No     Result     Result                   Ratio
-------------------------------------------------------------
  1     17  1       .2224     2.1000                   9.44
  2     24  1       .1441      .7800                   5.41
  3      1  1      7.9253     1.0300                    .13
  3      2  1      7.9253      .6000                    .08
  3      6  1      7.9253      .9000                    .11
  3      8  1      7.9253      .4000                    .05
  3     10  1      7.9253      .4000                    .05
  3     11  1      7.9253      .4000                    .05
  3     15  1      7.9253      .5000                    .06
  3     17  1      7.9253   127.0000                  16.02
  3     20  1      7.9253      .6000                    .08
  3     21  1      7.9253      .3000                    .04
  3     22  1      7.9253      .5100                    .06
  3     24  1      7.9253      .6900                    .09
  3     25  1      7.9253      .5000                    .06
  3     26  1      7.9253      .4000                    .05
  3     27  1      7.9253      .5000                    .06
-------------------------------------------------------------
Total Number of Questionable Observations:    17


-------------------------------------------------------------
 ***        Results of Factor of 5 Error Check           ***
 ***          Questionable Data (All Values)             ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean                Mean    Obs
 Lev   No   No     Result     Result     Dev     Dev   Ratio
-------------------------------------------------------------
  1    17   1       .1923     2.1000     .285    1.908  6.70
  3    17   1      7.9244   127.0000   14.009  119.076  8.50
  4    17   1      1.4681     4.3000     .521    2.832  5.43
  6    16   1      4.1306      .0000     .822    4.131  5.03
-------------------------------------------------------------
Total Number of Questionable Observations:     4


File Name:  cd-8
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Freshwater
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
----------------------------------------------
 ***      Laboratory Ranking Results      ***
 ***   Two-Tailed 5% Significance Level   ***
 ***----------------------------------------***
 ***     Upper Critical Value:    135.0   ***
 ***     Lower Critical Value:     45.0   ***
----------------------------------------------

      Ranks
     -----------------------------------------------------------------------------
       Rank  Level  Level  Level  Level  Level  Level  Level  Level  Level  Level
Lab    Sums    1      2      3      4      5      6      7      8      9     10
---- -----------------------------------------------------------------------------
  1   162.0  16.00  15.00  16.00  15.00  16.00  16.00  17.00  17.00  17.00  17.00
  2   106.0   7.00   7.50  12.50  10.50  12.00  13.50  13.00  13.00   7.00  10.00
  6   140.5  10.50  14.00  15.00  16.00  15.00  17.00  14.00  14.00  16.00   9.00
  7    38.5   1.00   2.00   1.00   7.00   3.50   4.00   7.00   5.00   4.00   4.00
  8    43.5  14.50   4.00   5.50   5.00   3.50   2.50   2.00   2.00   2.50   2.00
 10    77.5   3.00   4.00   5.50  14.00   9.00   5.00  12.00   9.00   5.00  11.00
 11    72.5  10.50  11.50   5.50   5.00   6.50   6.00   5.50   7.50   9.00   5.50
 15    76.0  10.50  11.50   9.00   8.50   6.50   8.00   9.50   3.00   2.50   7.00
 16    20.0   5.00   6.00   2.00   1.00   1.00   1.00   1.00   1.00   1.00   1.00
 17   143.5  17.00  16.00  17.00  17.00  17.00  11.50   8.00  12.00  14.00  14.00
 20   127.5   7.00   7.50  12.50  12.00  13.00  13.50  16.00  16.00  15.00  15.00
 21    68.0   3.00   1.00   3.00   5.00   6.50   8.00   9.50   7.50  12.00  12.50
 22    65.5   7.00   9.00  11.00   3.00   6.50   8.00   5.50   4.00   6.00   5.50
 24   145.0  13.00  17.00  14.00  13.00  14.00  15.00  15.00  15.00  13.00  16.00
 25    86.0  10.50  11.50   9.00   8.50  10.00  10.00   4.00  10.50   9.00   3.00
 26    90.5   3.00   4.00   5.50  10.50  11.00  11.50  11.00  10.50  11.00  12.50
 27    67.5  14.50  11.50   9.00   2.00   2.00   2.50   3.00   6.00   9.00   8.00
-------------------------------------------------
 *** Laboratory  24 Rejected; Rank Sum  145.0 ***
 *** Laboratory  16 Rejected; Rank Sum   20.0 ***
 *** Laboratory   1 Rejected; Rank Sum  162.0 ***
-------------------------------------------------
```

```
File Name:  cd-8
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Freshwater
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------
 ***    Outlier Testing Results      ***
 *** Two-Sided 5% Significance Level ***
-----------------------------------------

--------------------
   - Outlier(s) -
--------------------
 Lev  Iter  Lab  Rep     Result       Mean    Std Dev    t     Crit t   n
----------------------------------------------------------------------------
  1     1    17   1      2.1000      .1850      .5701   3.359   2.507   14
  3     1    17   1    127.0000     9.4999    33.8194   3.474   2.507   14
  4     1    17   1      4.3000     1.5193      .8576   3.242   2.507   14
  5     1    17   1      5.4000     3.5214      .7277   2.582   2.507   14
----------------------------------------------------------------------------
```

```
File Name:  cd-8
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Freshwater
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------
 *** Results of Normality Testing ***
-------------------------------------------

-------------------------
   - Normality Tests -
-------------------------
               Test  Normality      Test          Critical
   Level  n    Type  Accept/Reject  Statistic     Value(s)
---------------------------------------------------------------
     1    13     W     A             .9255      .866   ---
     2    14     W            R        .8670      .874   ---
     3    13     W     A             .8977      .866   ---
     4    13     W            R        .7783      .866   ---
     5    13     W     A             .9381      .866   ---
     6    14     W            R        .8683      .874   ---
     7    14     W     A             .9012      .874   ---
     8    14     W     A             .9692      .874   ---
     9    14     W            R        .7954      .874   ---
    10    14     W     A             .9764      .874   ---
-------------------------------
 - 4 Normality Rejection(s) -
-------------------------------
```

```
File Name:  cd-8
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Freshwater
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------------
 ***         Data Removal Tracking         ***
 *** Simple Count of Remaining Data Points ***
 ***          After Removal Tests          ***
-----------------------------------------------

             Points   After Lab Ranking  After Outlier Testing
               As     -----------------  ---------------------
 Lev  Mtrx  Received     Points    %         Points       %

 ---  ----  --------  ---------  ------  ----------     ------
  1    8      17         14    82.4         13       76.5
  2    8      17         14    82.4         14       82.4
  3    8      17         14    82.4         13       76.5
  4    8      17         14    82.4         13       76.5
  5    8      17         14    82.4         13       76.5
  6    8      17         14    82.4         14       82.4
  7    8      17         14    82.4         14       82.4
  8    8      17         14    82.4         14       82.4
  9    8      17         14    82.4         14       82.4
 10    8      17         14    82.4         14       82.4
 ---  ----  --------  ---------  ------  ----------     ------
Totals:        170         140    82.4        136       80.0
--------------------------------------------------------------
```

```
File Name:  cd-8
Statistical Analysis File (.STT)


----------------------------------------
 *** Summary Performance Statistics ***
----------------------------------------
Analyte:  Cd          Matrix:  Freshwater
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

------------------------------------------------------------------------------------------------------------------------
            LEVEL:         1         2         3         4         5         6         7         8         9        10
------------------------------------------------------------------------------------------------------------------------
YOUDEN PAIRS:         Pair 1    Pair 1    Pair 2    Pair 2    Pair 3    Pair 3    Pair 4    Pair 4    Pair 5    Pair 5
                       (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)
------------------------------------------------------------------------------------------------------------------------
CONCENTRATION:         .0436     .0436     .4436    1.1436    3.0436    3.8436    5.4436    7.0436    8.6436   10.3436
------------------------------------------------------------------------------------------------------------------------
RECOVERY:
 Observations             13        14        13        13        13        14        14        14        14        14
 Mean Result           .0377     .0491     .4614    1.3054    3.3769    4.2493    5.8779    7.7407    9.1679   10.8821
 Bias                 -.0059     .0055     .0178     .1618     .3333     .4057     .4343     .6971     .5243     .5385
 Relative Bias %    -13.5497   12.7130    4.0092   14.1470   10.9516   10.5548    7.9774    9.8971    6.0653    5.2065
 Maximum Result        .3000     .5000     .9000    2.2000    4.5000    5.9000    7.4000    9.9000   12.3000   14.0000
 Minimum Result       -.2100    -.1500    -.0120    1.0000    2.7000    3.5000    4.8000    6.0000    7.7000    8.0000
------------------------------------------------------------------------------------------------------------------------
SINGLE OPERATOR PRECISION:   Pair 1              Pair 2              Pair 3              Pair 4              Pair 5
   Observations                  13                  13                  13                  14                  14
   Standard Deviation         .1013               .1699               .2232               .4470               .9160
   Correction Factor         1.0210              1.0210              1.0210              1.0194              1.0194
   Corrected Std Dev          .1035               .1735               .2279               .4556               .9338
   Relative Std Dev (%)    237.1734             19.6360              5.9525              6.6913              9.3148
------------------------------------------------------------------------------------------------------------------------
OVERALL PRECISION:
 Observations              13        14        13        13        13        14        14        14        14        14
 Standard Deviation     .1516     .1809     .2047     .3208     .5069     .7185     .8679    1.1135    1.5352    1.5723
 Correction Factor     1.0210    1.0194    1.0210    1.0210    1.0210    1.0194    1.0194    1.0194    1.0194    1.0194
 Corrected Std Dev      .1547     .1844     .2090     .3276     .5175     .7325     .8848    1.1351    1.5650    1.6028
 Relative Std Dev %  410.5423  375.1765   45.3009   25.0936   15.3255   17.2379   15.0528   14.6642   17.0701   14.7288
------------------------------------------------------------------------------------------------------------------------
```

```
File Name:  cd-8
Statistical Analysis File (.STT)


----------------------------------
  *** Results of Bias Testing ***
----------------------------------
 Analyte:  Cd          Matrix:  Freshwater
 Project:  AMQ-TC      Method:  GFAAS
    Date:  12/13/1995
   Units:  ug/L

------------------------------------------------------------------------
                                    Rel.    Obs     Crit   Statistically
Conc.             Mean              Bias      t        t     Significant
Level   Conc    Result      Bias     (%)  Value    Value   (1% Two-Tail)
------------------------------------------------------------------------
 1     .0436     .0377    -.0059  -13.55    .140   3.055         NO
 2     .0436     .0491     .0055   12.71    .115   3.012         NO
 3     .4436     .4614     .0178    4.01    .313   3.055         NO
 4    1.1436    1.3054     .1618   14.15   1.818   3.055         NO
 5    3.0436    3.3769     .3333   10.95   2.371   3.055         NO
 6    3.8436    4.2493     .4057   10.55   2.113   3.012         NO
 7    5.4436    5.8779     .4343    7.98   1.872   3.012         NO
 8    7.0436    7.7407     .6971    9.90   2.342   3.012         NO
 9    8.6436    9.1679     .5243    6.07   1.278   3.012         NO
10   10.3436   10.8821     .5385    5.21   1.282   3.012         NO
------------------------------------------------------------------------
```

```
File Name:  cd-8
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***   Single Operator Precision    ***
----------------------------------------
Analyte:  Cd          Matrix:  Freshwater
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):      .1025
          Slope (b):      .0654
    =============================
                                        Single
           Sample Weights              Operator   Estimated
    Pair   Size       (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      13     80.47       .0436       .1035       .1054
      2      13     16.55       .7936       .1735       .1544
      3      13      1.93      3.4436       .2279       .3276
      4      14       .73      6.2436       .4556       .5106
      5      14       .33      9.4936       .9338       .7230
    -----------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    =========================================================
      a:      .1180      Intercept (a'):    -2.1371
      b:     1.2417          Slope (b'):      .2165
    =========================================================
                                               Single
           Sample Weight               Operator   Estimated
    Pair   Size      (%)        Conc     Std Dev     Std Dev
    ---------------------------------------------------------
      1      13    19.34       .0436       .1035       .1191
      2      13    19.34       .0436       .1735       .1401
      3      13    19.34       .4436       .2279       .2487
      4      14    20.99      1.1436       .4556       .4559
      5      14    20.99      3.0436       .9338       .9212
    ---------------------------------------------------------
```

```
File Name:  cd-8
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***       Overall Precision        ***
----------------------------------------
Analyte:  Cd          Matrix:  Freshwater
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Overall Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):      .1601
          Slope (b):      .1410
    =============================
    Conc   Sample   Weights                 Overall   Estimated
    Level  Size        (%)        Conc     Std Dev     Std Dev
    -------------------------------------------------------------
      1      13       33.12       .0436       .1547       .1662
      2      14       35.94       .0436       .1844       .1662
      3      13       17.18       .4436       .2090       .2226
      4      13        7.74      1.1436       .3276       .3214
      5      13        2.16      3.0436       .5175       .5893
      6      14        1.63      3.8436       .7325       .7021
      7      14         .92      5.4436       .8848       .9278
      8      14         .59      7.0436      1.1351      1.1534
      9      14         .41      8.6436      1.5650      1.3791
     10      14         .30     10.3436      1.6028      1.6188
    -------------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    ===========================================================
      a:      .2147      Intercept (a'):    -1.5386
      b:     1.2555          Slope (b'):      .2276
    ===========================================================
    Conc   Sample   Weight                 Overall   Estimated
    Level  Size       (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      13        9.52       .0436       .1547       .2168
      2      14       10.32       .0436       .1844       .2168
      3      13        9.52       .4436       .2090       .2375
      4      13        9.52      1.1436       .3276       .2785
      5      13        9.52      3.0436       .5175       .4291
      6      14       10.32      3.8436       .7325       .5148
      7      14       10.32      5.4436       .8848       .7409
      8      14       10.32      7.0436      1.1351      1.0664
      9      14       10.32      8.6436      1.5650      1.5348
     10      14       10.32     10.3436      1.6028      2.2597
    -----------------------------------------------------------
```

```
File Name:  cd-8
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ************  Recovery  **************
----------------------------------------
Analyte:  Cd          Matrix:  Freshwater
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Recovery ***

    - Linear Model - X = b*T + a
    =============================
      Intercept (a):      .0020
          Slope (b):     1.0834
    =============================
    Conc   Sample   Weights                  Mean   Estimated
    Level  Size         (%)      Conc      Result      Result
    ----------------------------------------------------------
      1      13     31.99       .0436       .0377       .0492
      2      14     34.45       .0436       .0491       .0492
      3      13     17.83       .4436       .4614       .4825
      4      13      8.56      1.1436      1.3054      1.2409
      5      13      2.55      3.0436      3.3769      3.2993
      6      14      1.93      3.8436      4.2493      4.1660
      7      14      1.11      5.4436      5.8779      5.8994
      8      14       .72      7.0436      7.7407      7.6328
      9      14       .50      8.6436      9.1679      9.3662
     10      14       .36     10.3436     10.8821     11.2079
    ----------------------------------------------------------
```

```
File Name:  cd-8
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***     Precision vs Recovery      ***
----------------------------------------
Analyte:  Cd          Matrix:  Freshwater
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision vs Recovery ***
           (Obtained by Substitution)

     - Linear Model - s = f*X + e
    ==============================
        Intercept (e):      .1007
            Slope (f):      .0603
    ==============================


     - Curvilinear Model - s = e*(f**X)
    ====================================
        Intercept (e):      .1179
                  (f):     1.2212
    ====================================



 *** Overall Precision vs Recovery ***
       (Obtained by Substitution)

     - Linear Model - s = f*X + e
     =============================
        Intercept (e):      .1583
            Slope (f):      .1302
     =============================


     - Curvilinear Model - s = e*(f**X)
     ===================================
        Intercept (e):      .2146
                  (f):     1.2337
     ===================================
```

```
cd-9.dat

Cd     9   6     2.0000    2.0000   14.0000   24.0000   43.0000   53.0000   69.0000   82.0000   86.0000   94.0000
Cd     9   7    -0.5090   -0.3070    8.7100   13.1000   27.6000   37.8000   43.9000   59.0000   83.4000   92.2000
Cd     9   8     2.3000    2.5000   10.4000   13.3000   31.0000   31.7000   41.5000   52.3000   71.6000   79.9000
Cd     9  10     0.0000    0.0000    2.0000    5.5000    2.4500   12.0000   15.0000   35.0000   32.6000   95.5000
Cd     9  15     0.1000    0.1000    9.0000   15.0000   30.0000   41.0000   51.0000   62.0000   91.0000  104.0000
Cd     9  16    -0.0020   -0.0020    1.0000    0.0000   22.2000   22.2000   44.4000   44.4000  128.0000   88.8000
Cd     9  17     0.1000    0.3000    6.4000   10.6000   33.2000   33.0000   43.0000   59.0000   77.0000   91.0000
Cd     9  20     0.0000    0.0000   11.0000   19.0000   34.0000   45.0000   58.0000   74.0000  107.0000  121.0000
Cd     9  21    -0.3000    0.0000    8.9000   16.9000   33.0000   44.8000   65.7000   65.0000   91.8000  103.8000
Cd     9  22     0.0600    0.0600    9.3000   14.2000   29.0000   36.4000   45.6000   57.2000   81.2000   92.0000
Cd     9  24     0.9000    1.1000   10.7000   19.1000   39.8000   53.5000   69.0000   69.2000  149.0000  105.0000
Cd     9  25     0.0000    0.0000    8.5000   16.4000   28.7000   38.5000   54.5000   65.7000   87.9000  113.0000
Cd     9  26    -0.1000   -1.0000   11.0000   19.0000   36.0000   45.0000   55.0000   70.0000   90.0000  110.0000
Cd     9  27     0.0000    3.0000    4.0000    4.0000    9.0000   14.0000   16.0000   23.0000   34.0000   42.0000
```

```
File Name:  cd-9
Data Validation File (.DA~)

******************************************************************************
***                   Parameter and Data Validation File                   ***
******************************************************************************
   Analyte:  Cd              Matrix:  Estuarine
   Project:  AMQ-TC       Matrix ID:   9
      Date:  12/13/1995      Method:  GFAAS
     Pairs:  5
     Units:  ug/L

---------------------------------------------------------------------------------------------------------------------------------
Level          1          2            3          4            5          6            7          8            9         10
---------------------------------------------------------------------------------------------------------------------------------
Spike          .1739      .0000       9.2000     6.0000      14.7000     9.5000       9.6000    12.3000      24.6000    11.0000
Spike
Increment      .0000      .0000       9.2000    15.2000      29.9000    39.4000      49.0000    61.3000      85.9000    96.9000
---------------------------------------------------------------------------------------------------------------------------------

                 Final Concentration
         ------------------------------------------------------------------------------------------------------------------------
Lab ID         .1739      .1739       9.3739    15.3739      30.0739    39.5739      49.1739    61.4739      86.0739    97.0739
---------------------------------------------------------------------------------------------------------------------------------
    6    r    2.0000r    2.0000  r   14.0000r   24.0000  r   43.0000r   53.0000  r   69.0000r   82.0000  r   86.0000r   94.0000
    7    ?    -.5090     -.3070       8.7100    13.1000      27.6000    37.8000      43.9000    59.0000      83.4000    92.2000
    8    o    2.3000     2.5000      10.4000    13.3000      31.0000    31.7000      41.5000    52.3000      71.6000    79.9000
   10    !     .0000!     .0000  !    2.0000!    5.5000  !    2.4500!   12.0000  !   15.0000!   35.0000  !   32.6000!   95.5000
   15          .1000      .1000       9.0000    15.0000      30.0000    41.0000      51.0000    62.0000      91.0000   104.0000
   16         -.0020     -.0020       1.0000      .0000      22.2000    22.2000      44.4000    44.4000     128.0000    88.8000
   17          .1000      .3000       6.4000    10.6000      33.2000    33.0000      43.0000    59.0000      77.0000    91.0000
   20          .0000      .0000      11.0000    19.0000      34.0000    45.0000      58.0000    74.0000     107.0000   121.0000
   21         -.3000      .0000       8.9000    16.9000      33.0000    44.8000      65.7000    65.0000      91.8000   103.8000
   22          .0600      .0600       9.3000    14.2000      29.0000    36.4000      45.6000    57.2000      81.2000    92.0000
   24    r     .9000r    1.1000  r   10.7000r   19.1000  r   39.8000r   53.5000  r   69.0000r   69.2000  r  149.0000r  105.0000
   25          .0000      .0000       8.5000    16.4000      28.7000    38.5000      54.5000    65.7000      87.9000   113.0000
   26         -.1000    -1.0000      11.0000    19.0000      36.0000    45.0000      55.0000    70.0000      90.0000   110.0000
   27    !     .0000!    3.0000  !    4.0000!    4.0000  !    9.0000!   14.0000  !   16.0000!   23.0000  !   34.0000o   42.0000
---------------------------------------------------------------------------------------------------------------------------------
```

```
cd-9.daf

Cd     9   7     -.5090    -.3070    8.7100   13.1000   27.6000   37.8000   43.9000   59.0000   83.4000   92.2000
Cd     9   8 o             2.5000   10.4000   13.3000   31.0000   31.7000   41.5000   52.3000   71.6000   79.9000
Cd     9  10      .0000     .0000    2.0000    5.5000    2.4500   12.0000   15.0000   35.0000   32.6000   95.5000
Cd     9  15      .1000     .1000    9.0000   15.0000   30.0000   41.0000   51.0000   62.0000   91.0000  104.0000
Cd     9  16     -.0020    -.0020    1.0000     .0000   22.2000   22.2000   44.4000   44.4000  128.0000   88.8000
Cd     9  17      .1000     .3000    6.4000   10.6000   33.2000   33.0000   43.0000   59.0000   77.0000   91.0000
Cd     9  20      .0000     .0000   11.0000   19.0000   34.0000   45.0000   58.0000   74.0000  107.0000  121.0000
Cd     9  21     -.3000     .0000    8.9000   16.9000   33.0000   44.8000   65.7000   65.0000   91.8000  103.8000
Cd     9  22      .0600     .0600    9.3000   14.2000   29.0000   36.4000   45.6000   57.2000   81.2000   92.0000
Cd     9  25      .0000     .0000    8.5000   16.4000   28.7000   38.5000   54.5000   65.7000   87.9000  113.0000
Cd     9  26     -.1000   -1.0000   11.0000   19.0000   36.0000   45.0000   55.0000   70.0000   90.0000  110.0000
Cd     9  27      .0000    3.0000    4.0000    4.0000    9.0000   14.0000   16.0000   23.0000   34.0000o
```

```
File Name:  cd-9
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Estuarine
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------------------------
 ***        Results of 5x - 1/5x Mean Error Check        ***
 ***         Questionable Data (Positive Values)         ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean
 Lev   No   No     Result     Result                   Ratio
-------------------------------------------------------------
  1      6  1       .3900     2.0000                   5.13
  1      8  1       .3900     2.3000                   5.90
  1     22  1       .3900      .0600                    .15
  2     15  1       .6471      .1000                    .15
  2     22  1       .6471      .0600                    .09
  3     16  1      8.2079     1.0000                    .12
  5     10  1     28.4964     2.4500                    .09
-------------------------------------------------------------
Total Number of Questionable Observations:     7


-------------------------------------------------------------
 ***        Results of Factor of 5 Error Check           ***
 ***          Questionable Data (All Values)             ***
-------------------------------------------------------------
Total Number of Questionable Observations:     0
```

```
File Name:  cd-9
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Estuarine
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
----------------------------------------------
 ***      Laboratory Ranking Results      ***
 ***   Two-Tailed 5% Significance Level   ***
 ***--------------------------------------***
 ***     Upper Critical Value:    112.0   ***
 ***     Lower Critical Value:     38.0   ***
----------------------------------------------

      Ranks
     -----------------------------------------------------------------------------
       Rank  Level  Level  Level  Level  Level  Level  Level  Level  Level  Level
Lab    Sums    1      2      3      4      5      6      7      8      9     10
---- -----------------------------------------------------------------------------
  6   121.5  13.00  12.00  14.00  14.00  14.00  13.00  13.50  14.00   7.00   7.00
  7    48.5   1.00   2.00   6.00   5.00   4.00   7.00   5.00   6.50   6.00   6.00
  8    67.0  14.00  13.00  10.00   6.00   8.00   4.00   3.00   4.00   3.00   2.00
 10    31.0   6.50   5.50   2.00   3.00   1.00   1.00   1.00   2.00   1.00   8.00
 15    87.5  10.50   9.00   8.00   8.00   7.00   9.00   8.00   8.00  10.00  10.00
 16    40.0   4.00   3.00   1.00   1.00   3.00   3.00   6.00   3.00  13.00   3.00
 17    62.0  10.50  10.00   4.00   4.00  10.00   5.00   4.00   6.50   4.00   4.00
 20   108.5   6.50   5.50  12.50  11.50  11.00  11.50  11.00  13.00  12.00  14.00
 21    84.5   2.00   5.50   7.00  10.00   9.00  10.00  12.00   9.00  11.00   9.00
 22    67.0   9.00   8.00   9.00   7.00   6.00   6.00   7.00   5.00   5.00   5.00
 24   123.5  12.00  11.00  11.00  13.00  13.00  14.00  13.50  11.00  14.00  11.00
 25    79.0   6.50   5.50   5.00   9.00   5.00   8.00   9.00  10.00   8.00  13.00
 26    94.5   3.00   1.00  12.50  11.50  12.00  11.50  10.00  12.00   9.00  12.00
 27    35.5   6.50  14.00   3.00   2.00   2.00   2.00   2.00   1.00   2.00   1.00
-------------------------------------------------
 *** Laboratory   6 Rejected; Rank Sum  121.5 ***
 *** Laboratory  24 Rejected; Rank Sum  123.5 ***
-------------------------------------------------
```

```
File Name:  cd-9
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Estuarine
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------
 ***    Outlier Testing Results      ***
 *** Two-Sided 5% Significance Level ***
-----------------------------------------

--------------------
   - Outlier(s) -
--------------------
 Lev  Iter  Lab  Rep     Result       Mean    Std Dev    t     Crit t   n
----------------------------------------------------------------------------
  1     1     8   1      2.3000      .1374      .7036   3.073   2.412   12
  *     1    27   1     42.0000    94.4333    20.1993   2.596   2.412   12
----------------------------------------------------------------------------
```

```
File Name:  cd-9
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Estuarine
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------
 *** Results of Normality Testing ***
-------------------------------------------

-------------------------
   - Normality Tests -
-------------------------
               Test  Normality      Test          Critical
   Level  n    Type  Accept/Reject  Statistic     Value(s)
---------------------------------------------------------------
     1    11     W            R       .7562      .850   ---
     2    12     W            R       .7060      .859   ---
     3    12     W            R       .8531      .859   ---
     4    12     W     A              .8989      .859   ---
     5    12     W            R       .7804      .859   ---
     6    12     W     A              .8648      .859   ---
     7    12     W     A              .8712      .859   ---
     8    12     W     A              .9110      .859   ---
     9    12     W     A              .9030      .859   ---
    10    11     W     A              .9626      .850   ---
-------------------------------
 - 4 Normality Rejection(s) -
-------------------------------


File Name:  cd-9
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Estuarine
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------------
 ***         Data Removal Tracking         ***
 *** Simple Count of Remaining Data Points ***
 ***          After Removal Tests          ***
-----------------------------------------------

             Points   After Lab Ranking  After Outlier Testing
               As     -----------------  ---------------------
 Lev  Mtrx  Received     Points    %         Points       %

 ---  ----  --------  ---------  ------  ----------     ------
  1     9       14          12    85.7          11       78.6
  2     9       14          12    85.7          12       85.7
  3     9       14          12    85.7          12       85.7
  4     9       14          12    85.7          12       85.7
  5     9       14          12    85.7          12       85.7
  6     9       14          12    85.7          12       85.7
  7     9       14          12    85.7          12       85.7
  8     9       14          12    85.7          12       85.7
  9     9       14          12    85.7          12       85.7
 10     9       14          12    85.7          11       78.6
 ---  ----  --------  ---------  ------  ----------     ------
Totals:        140         120    85.7         118       84.3
---------------------------------------------------------------
```

```
File Name:  cd-9
Statistical Analysis File (.STT)


----------------------------------------
 *** Summary Performance Statistics ***
----------------------------------------
Analyte:  Cd          Matrix:  Estuarine
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

------------------------------------------------------------------------------------------------------------------------
            LEVEL:         1         2         3         4         5         6         7         8         9        10
------------------------------------------------------------------------------------------------------------------------
YOUDEN PAIRS:         Pair 1    Pair 1    Pair 2    Pair 2    Pair 3    Pair 3    Pair 4    Pair 4    Pair 5    Pair 5
                       (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)
------------------------------------------------------------------------------------------------------------------------
CONCENTRATION:         .1739     .1739    9.3739   15.3739   30.0739   39.5739   49.1739   61.4739   86.0739   97.0739
------------------------------------------------------------------------------------------------------------------------
RECOVERY:
 Observations             11        12        12        12        12        12        12        12        12        11
 Mean Result          -.0592     .3876    7.5175   12.2500   26.3458   33.4500   44.4667   55.5500   81.2917   99.2000
 Bias                 -.2331     .2137   -1.8564   -3.1239   -3.7281   -6.1239   -4.7072   -5.9239   -4.7822    2.1261
 Relative Bias %   -134.0321  122.8771  -19.8039  -20.3195  -12.3963  -15.4746   -9.5726   -9.6364   -5.5560    2.1902
 Maximum Result        .1000    3.0000   11.0000   19.0000   36.0000   45.0000   65.7000   74.0000  128.0000  121.0000
 Minimum Result       -.5090   -1.0000    1.0000     .0000    2.4500   12.0000   15.0000   23.0000   32.6000   79.9000
------------------------------------------------------------------------------------------------------------------------
SINGLE OPERATOR PRECISION:   Pair 1              Pair 2              Pair 3              Pair 4              Pair 5
   Observations                  11                  12                  12                  12                  11
   Standard Deviation         .6807              2.1767              3.2205              4.4622             16.5133
   Correction Factor         1.0253              1.0230              1.0230              1.0230              1.0253
   Corrected Std Dev          .6979              2.2266              3.2945              4.5647             16.9306
   Relative Std Dev (%)    401.2945             22.5282             11.0191              9.1278             18.8418
------------------------------------------------------------------------------------------------------------------------
OVERALL PRECISION:
 Observations              11        12        12        12        12        12        12        12        12        11
 Standard Deviation     .1855    1.1539    3.4216    6.1019   10.3630   11.5758   15.3134   14.8518   26.7836   12.2023
 Correction Factor     1.0253    1.0230    1.0230    1.0230    1.0230    1.0230    1.0230    1.0230    1.0230    1.0253
 Corrected Std Dev      .1902    1.1803    3.5001    6.2420   10.6008   11.8415   15.6650   15.1928   27.3984   12.5107
 Relative Std Dev % -321.3881  304.5391   46.5599   50.9552   40.2373   35.4007   35.2285   27.3497   33.7038   12.6115
------------------------------------------------------------------------------------------------------------------------
```

```
File Name:  cd-9
Statistical Analysis File (.STT)


----------------------------------
  *** Results of Bias Testing ***
----------------------------------
 Analyte:  Cd          Matrix:  Estuarine
 Project:  AMQ-TC      Method:  GFAAS
    Date:  12/13/1995
   Units:  ug/L

------------------------------------------------------------------------
                                    Rel.   Obs     Crit   Statistically
Conc.             Mean              Bias      t       t     Significant
Level   Conc     Result      Bias     (%)   Value   Value   (1% Two-Tail)
------------------------------------------------------------------------
 1     .1739    -.0592    -.2331  ******   4.166   3.169        YES
 2     .1739     .3876     .2137  122.88    .642   3.106         NO
 3    9.3739    7.5175   -1.8564  -19.80   1.879   3.106         NO
 4   15.3739   12.2500   -3.1239  -20.32   1.773   3.106         NO
 5   30.0739   26.3458   -3.7281  -12.40   1.246   3.106         NO
 6   39.5739   33.4500   -6.1239  -15.47   1.833   3.106         NO
 7   49.1739   44.4667   -4.7072   -9.57   1.065   3.106         NO
 8   61.4739   55.5500   -5.9239   -9.64   1.382   3.106         NO
 9   86.0739   81.2917   -4.7822   -5.56    .619   3.106         NO
10   97.0739   99.2000    2.1261    2.19    .578   3.169         NO
------------------------------------------------------------------------
```

```
File Name:  cd-9
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***   Single Operator Precision    ***
----------------------------------------
Analyte:  Cd          Matrix:  Estuarine
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):      .7771
          Slope (b):      .0888
    =============================
                                           Single
           Sample Weights               Operator   Estimated
    Pair   Size       (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      11     58.88       .1739       .6979       .7925
      2      12     30.82     12.3739      2.2266      1.8759
      3      12      7.83     34.8239      3.2945      3.8695
      4      12      2.24     55.3239      4.5647      5.6899
      5      11       .22     91.5739     16.9306      8.9089
    -----------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    =========================================================
      a:     1.0176      Intercept (a'):      .0174
      b:     1.0310          Slope (b'):      .0305
    =========================================================
                                                  Single
           Sample Weight               Operator   Estimated
    Pair   Size      (%)        Conc     Std Dev     Std Dev
    ---------------------------------------------------------
      1      11    18.84       .1739       .6979      1.0230
      2      12    20.77       .1739      2.2266      1.4843
      3      12    20.77      9.3739      3.2945      2.9444
      4      12    20.77     15.3739      4.5647      5.5034
      5      11    18.84     30.0739     16.9306     16.6323
    ---------------------------------------------------------

File Name:  cd-9
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***      Overall Precision        ***
----------------------------------------
Analyte:  Cd          Matrix:  Estuarine
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Overall Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):      .8957
          Slope (b):      .2629
    =============================
    Conc   Sample   Weights                  Overall   Estimated
    Level  Size         (%)        Conc     Std Dev     Std Dev
    -------------------------------------------------------------
      1      11       33.25       .1739       .1902       .9415
      2      12       36.65       .1739      1.1803       .9415
      3      12       12.66      9.3739      3.5001      3.3597
      4      12        7.86     15.3739      6.2420      4.9369
      5      12        3.41     30.0739     10.6008      8.8009
      6      12        2.28     39.5739     11.8415     11.2980
      7      12        1.63     49.1739     15.6650     13.8214
      8      12        1.14     61.4739     15.1928     17.0546
      9      12         .64     86.0739     27.3984     23.5209
     10      11         .47     97.0739     12.5107     26.4123
    -------------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    ===========================================================
      a:     1.7061      Intercept (a'):      .5342
      b:     1.0332          Slope (b'):      .0327
    ===========================================================
    Conc   Sample   Weight                  Overall   Estimated
    Level  Size        (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      11       9.24       .1739       .1902      1.7158
      2      12      10.19       .1739      1.1803      1.7158
      3      12      10.19      9.3739      3.5001      2.3180
      4      12      10.19     15.3739      6.2420      2.8204
      5      12      10.19     30.0739     10.6008      4.5608
      6      12      10.19     39.5739     11.8415      6.2221
      7      12      10.19     49.1739     15.6650      8.5163
      8      12      10.19     61.4739     15.1928     12.7322
      9      12      10.19     86.0739     27.3984     28.4584
     10      11       9.24     97.0739     12.5107     40.7760
    -----------------------------------------------------------
```

```
File Name:  cd-9
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ************  Recovery  **************
----------------------------------------
Analyte:  Cd          Matrix:  Estuarine
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Recovery ***

    - Linear Model - X = b*T + a
    ============================
      Intercept (a):     -.0421
          Slope (b):      .8961
    ============================
    Conc   Sample   Weights                  Mean   Estimated
    Level  Size         (%)      Conc      Result      Result
    ----------------------------------------------------------
      1      11     44.49       .1739      -.0592       .1137
      2      12     48.53       .1739       .3876       .1137
      3      12      3.81      9.3739      7.5175      8.3576
      4      12      1.77     15.3739     12.2500     13.7341
      5      12       .56     30.0739     26.3458     26.9064
      6      12       .34     39.5739     33.4500     35.4191
      7      12       .23     49.1739     44.4667     44.0215
      8      12       .15     61.4739     55.5500     55.0432
      9      12       .08     86.0739     81.2917     77.0867
     10      11       .06     97.0739     99.2000     86.9436
    ----------------------------------------------------------


File Name:  cd-9
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***     Precision vs Recovery      ***
----------------------------------------
Analyte:  Cd          Matrix:  Estuarine
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision vs Recovery ***
           (Obtained by Substitution)

     - Linear Model - s = f*X + e
    ==============================
        Intercept (e):      .8241
            Slope (f):      .0991
    ==============================


     - Curvilinear Model - s = e*(f**X)
    ====================================
        Intercept (e):     1.0191
                  (f):     1.0346
    ====================================



 *** Overall Precision vs Recovery ***
       (Obtained by Substitution)

     - Linear Model - s = f*X + e
     =============================
        Intercept (e):      .9428
            Slope (f):      .2933
     =============================


     - Curvilinear Model - s = e*(f**X)
     ===================================
        Intercept (e):     1.7087
                  (f):     1.0372
     ===================================
```

```
cd-10.dat

Cd    10   1     7.0000    7.0000   31.5000   46.4000   67.3000   75.1000   97.8000  106.4000  145.0000  158.2000
Cd    10   2     5.1000    3.9000   19.8000   29.1000   42.6000   51.6000   69.2000   78.3000   81.0000   88.0000
Cd    10   6     6.0000    7.0000   30.0000   39.0000   60.0000   73.0000   87.0000   94.0000   84.0000   87.0000
Cd    10   7     3.6700    2.9800  -10.6000  -11.3000   -6.7500  -10.9000   -5.2100   -9.4300    0.8220   -6.3600
Cd    10   8     3.1000    2.7000   18.0000   24.1000   32.5000   39.5000   48.4000   55.3000   66.7000   73.9000
Cd    10  10     2.0000    2.0000   24.0000   31.0000   50.5000   58.5000   71.0000   87.0000   92.0000  104.5000
Cd    10  11     3.7000    3.7000   20.7000   28.0000   39.7000   47.7000   63.5000   69.0000   84.0000   90.5000
Cd    10  15     3.0000    3.0000   20.0000   29.0000   40.0000   48.0000   59.0000   61.0000   80.0000   97.0000
Cd    10  16     0.0000    0.0000   22.2000   15.6000   22.2000   37.8000   44.4000   60.0000   33.3000   73.0000
Cd    10  17     4.3000    4.0000   26.0000   26.0000   43.0000   46.0000   64.0000   70.0000   78.0000  122.0000
Cd    10  20     5.0000    4.0000   23.0000   32.0000   46.0000   57.0000   77.0000   86.0000  106.0000  115.0000
Cd    10  21     3.4000    3.7000   21.3000   45.7000   45.2000   61.7000   77.1000   79.8000   87.5000   96.0000
Cd    10  24     3.7000    3.5000   21.1000   29.4000   43.9000   54.2000   75.5000   79.9000  103.0000  112.0000
Cd    10  25     3.6000    2.6000   20.6000   29.5000   41.8000   48.0000   63.6000   77.8000   87.9000   97.0000
Cd    10  26     4.0000    5.0000   26.0000   33.0000   44.0000   49.0000   70.0000   80.0000   90.0000  100.0000
Cd    10  27     0.0000    0.0000    2.0000    0.0000    4.0000   20.0000    5.0000    4.0000   10.0000    6.0000
```

```
File Name:  cd-10
Data Validation File (.DA~)

******************************************************************************
***                   Parameter and Data Validation File                   ***
******************************************************************************
   Analyte:  Cd              Matrix:  Acid Mine Drainage
   Project:  AMQ-TC       Matrix ID:  10
      Date:  12/13/1995      Method:  GFAAS
     Pairs:  5
     Units:  ug/L

---------------------------------------------------------------------------------------------------------------------------------
Level          1          2            3          4            5          6            7          8            9         10
---------------------------------------------------------------------------------------------------------------------------------
Spike         3.5385      .0000      16.0000     8.5000      11.8000     8.1000      14.3000     8.7000      13.8000     8.1000
Spike
Increment      .0000      .0000      16.0000    24.5000      36.3000    44.4000      58.7000    67.4000      81.2000    89.3000
---------------------------------------------------------------------------------------------------------------------------------

                 Final Concentration
         ------------------------------------------------------------------------------------------------------------------------
Lab ID        3.5385     3.5385      19.5385    28.0385      39.8385    47.9385      62.2385    70.9385      84.7385    92.8385
---------------------------------------------------------------------------------------------------------------------------------
    1    r    7.0000r    7.0000  r   31.5000r   46.4000  r   67.3000r   75.1000  r   97.8000r  106.4000  r  145.0000r  158.2000
    2         5.1000     3.9000      19.8000    29.1000      42.6000    51.6000      69.2000    78.3000      81.0000    88.0000
    6    !    6.0000!    7.0000  !   30.0000!   39.0000  !   60.0000!   73.0000  !   87.0000!   94.0000  !   84.0000!   87.0000
    7    r    3.6700r    2.9800  r  -10.6000r  -11.3000  r   -6.7500r  -10.9000  r   -5.2100r   -9.4300  r     .8220r   -6.3600
    8    !    3.1000!    2.7000  !   18.0000!   24.1000  !   32.5000!   39.5000  !   48.4000!   55.3000  !   66.7000!   73.9000
   10         2.0000     2.0000      24.0000    31.0000      50.5000    58.5000      71.0000    87.0000      92.0000   104.5000
   11         3.7000     3.7000      20.7000    28.0000      39.7000    47.7000      63.5000    69.0000      84.0000    90.5000
   15         3.0000     3.0000      20.0000    29.0000      40.0000    48.0000      59.0000    61.0000      80.0000    97.0000
   16    !     .0000!     .0000  !   22.2000!   15.6000  !   22.2000!   37.8000  !   44.4000!   60.0000  o   33.3000!   73.0000
   17         4.3000     4.0000      26.0000    26.0000      43.0000    46.0000      64.0000    70.0000      78.0000   122.0000
   20    !    5.0000!    4.0000  !   23.0000!   32.0000  !   46.0000!   57.0000  !   77.0000!   86.0000  !  106.0000!  115.0000
   21         3.4000     3.7000      21.3000    45.7000      45.2000    61.7000      77.1000    79.8000      87.5000    96.0000
   24         3.7000     3.5000      21.1000    29.4000      43.9000    54.2000      75.5000    79.9000     103.0000   112.0000
   25         3.6000     2.6000      20.6000    29.5000      41.8000    48.0000      63.6000    77.8000      87.9000    97.0000
   26         4.0000     5.0000      26.0000    33.0000      44.0000    49.0000      70.0000    80.0000      90.0000   100.0000
   27    r     .0000r     .0000  r    2.0000r     .0000  r    4.0000r   20.0000  r    5.0000r    4.0000  r   10.0000r    6.0000
---------------------------------------------------------------------------------------------------------------------------------
```

```
cd-10.daf

Cd    10   2     5.1000    3.9000   19.8000   29.1000   42.6000   51.6000   69.2000   78.3000   81.0000   88.0000
Cd    10   6     6.0000    7.0000   30.0000   39.0000   60.0000   73.0000   87.0000   94.0000   84.0000   87.0000
Cd    10   8     3.1000    2.7000   18.0000   24.1000   32.5000   39.5000   48.4000   55.3000   66.7000   73.9000
Cd    10  10     2.0000    2.0000   24.0000   31.0000   50.5000   58.5000   71.0000   87.0000   92.0000  104.5000
Cd    10  11     3.7000    3.7000   20.7000   28.0000   39.7000   47.7000   63.5000   69.0000   84.0000   90.5000
Cd    10  15     3.0000    3.0000   20.0000   29.0000   40.0000   48.0000   59.0000   61.0000   80.0000   97.0000
Cd    10  16      .0000     .0000   22.2000   15.6000   22.2000   37.8000   44.4000   60.0000o            73.0000
Cd    10  17     4.3000    4.0000   26.0000   26.0000   43.0000   46.0000   64.0000   70.0000   78.0000  122.0000
Cd    10  20     5.0000    4.0000   23.0000   32.0000   46.0000   57.0000   77.0000   86.0000  106.0000  115.0000
Cd    10  21     3.4000    3.7000   21.3000   45.7000   45.2000   61.7000   77.1000   79.8000   87.5000   96.0000
Cd    10  24     3.7000    3.5000   21.1000   29.4000   43.9000   54.2000   75.5000   79.9000  103.0000  112.0000
Cd    10  25     3.6000    2.6000   20.6000   29.5000   41.8000   48.0000   63.6000   77.8000   87.9000   97.0000
Cd    10  26     4.0000    5.0000   26.0000   33.0000   44.0000   49.0000   70.0000   80.0000   90.0000  100.0000
```

```
File Name:  cd-10
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Acid Mine Drainage
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------------------------
 ***        Results of 5x - 1/5x Mean Error Check        ***
 ***         Questionable Data (Positive Values)         ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean
 Lev   No   No     Result     Result                   Ratio
-------------------------------------------------------------
  3     27  1     20.3875     2.0000                   .10
  5     27  1     38.9188     4.0000                   .10
  7     27  1     60.7812     5.0000                   .08
  8     27  1     68.0313     4.0000                   .06
  9      7  1     76.8264      .8220                   .01
  9     27  1     76.8264    10.0000                   .13
 10     27  1     88.7562     6.0000                   .07
-------------------------------------------------------------
Total Number of Questionable Observations:     7


-------------------------------------------------------------
 ***        Results of Factor of 5 Error Check           ***
 ***          Questionable Data (All Values)             ***
-------------------------------------------------------------
Total Number of Questionable Observations:     0


File Name:  cd-10
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Acid Mine Drainage
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
----------------------------------------------
 ***      Laboratory Ranking Results      ***
 ***   Two-Tailed 5% Significance Level   ***
 ***--------------------------------------***
 ***     Upper Critical Value:    127.0   ***
 ***     Lower Critical Value:     42.0   ***
----------------------------------------------

      Ranks
     -----------------------------------------------------------------------------
       Rank  Level  Level  Level  Level  Level  Level  Level  Level  Level  Level
Lab    Sums    1      2      3      4      5      6      7      8      9     10
---- -----------------------------------------------------------------------------
  1   159.5  16.00  15.50  16.00  16.00  16.00  16.00  16.00  16.00  16.00  16.00
  2    86.0  14.00  11.00   4.00   8.00   8.00  10.00   9.00   9.00   7.00   6.00
  6   133.0  15.00  15.50  15.00  14.00  15.00  15.00  15.00  15.00   8.50   5.00
  7    22.0   8.00   6.00   1.00   1.00   1.00   1.00   1.00   1.00   1.00   1.00
  8    40.0   5.00   5.00   3.00   4.00   4.00   4.00   4.00   3.00   4.00   4.00
 10   106.0   3.00   3.00  12.00  11.00  14.00  13.00  11.00  14.00  13.00  12.00
 11    70.5   9.50   9.50   7.00   6.00   5.00   6.00   6.00   6.00   8.50   7.00
 15    62.0   4.00   7.00   5.00   7.00   6.00   7.50   5.00   5.00   6.00   9.50
 16    35.0   1.50   1.50  10.00   3.00   3.00   3.00   3.00   4.00   3.00   3.00
 17    92.0  12.00  12.50  13.50   5.00   9.00   5.00   8.00   7.00   5.00  15.00
 20   128.5  13.00  12.50  11.00  12.00  13.00  12.00  13.00  13.00  15.00  14.00
 21   107.5   6.00   9.50   9.00  15.00  12.00  14.00  14.00  10.00  10.00   8.00
 24   105.5   9.50   8.00   8.00   9.00  10.00  11.00  12.00  11.00  14.00  13.00
 25    77.0   7.00   4.00   6.00  10.00   7.00   7.50   7.00   8.00  11.00   9.50
 26   116.5  11.00  14.00  13.50  13.00  11.00   9.00  10.00  12.00  12.00  11.00
 27    19.0   1.50   1.50   2.00   2.00   2.00   2.00   2.00   2.00   2.00   2.00
-------------------------------------------------
 *** Laboratory   7 Rejected; Rank Sum   22.0 ***
 *** Laboratory  27 Rejected; Rank Sum   19.0 ***
 *** Laboratory   1 Rejected; Rank Sum  159.5 ***
-------------------------------------------------

File Name:  cd-10
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Acid Mine Drainage
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------
 ***    Outlier Testing Results      ***
 *** Two-Sided 5% Significance Level ***
-----------------------------------------

--------------------
   - Outlier(s) -
--------------------
 Lev  Iter  Lab  Rep     Result       Mean    Std Dev    t     Crit t   n
----------------------------------------------------------------------------
  9     1    16   1     33.3000    82.5692    17.9737   2.741   2.462   13
----------------------------------------------------------------------------
```

```
File Name:  cd-10
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Acid Mine Drainage
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------
 *** Results of Normality Testing ***
-------------------------------------------

-------------------------
   - Normality Tests -
-------------------------
               Test  Normality      Test          Critical
   Level  n    Type  Accept/Reject  Statistic     Value(s)
-------------------------------------------------------------
     1    13     W     A              .9343      .866   ---
     2    13     W     A              .9341      .866   ---
     3    13     W     A              .9211      .866   ---
     4    13     W     A              .9268      .866   ---
     5    13     W     A              .9108      .866   ---
     6    13     W     A              .9498      .866   ---
     7    13     W     A              .9604      .866   ---
     8    13     W     A              .9501      .866   ---
     9    12     W     A              .9567      .859   ---
    10    13     W     A              .9673      .866   ---
-------------------------------
 - 0 Normality Rejection(s) -
-------------------------------
```

```
File Name:  cd-10
Data Preparation File (.PRP)


Analyte:  Cd     Matrix:  Acid Mine Drainage
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------------
 ***         Data Removal Tracking         ***
 *** Simple Count of Remaining Data Points ***
 ***          After Removal Tests          ***
-----------------------------------------------

             Points   After Lab Ranking  After Outlier Testing
               As     -----------------  ---------------------
 Lev  Mtrx  Received     Points    %         Points       %

 ---  ----  --------  ---------  ------  ----------     ------
  1    10       16          13    81.3          13       81.3
  2    10       16          13    81.3          13       81.3
  3    10       16          13    81.3          13       81.3
  4    10       16          13    81.3          13       81.3
  5    10       16          13    81.3          13       81.3
  6    10       16          13    81.3          13       81.3
  7    10       16          13    81.3          13       81.3
  8    10       16          13    81.3          13       81.3
  9    10       16          13    81.3          12       75.0
 10    10       16          13    81.3          13       81.3
 ---  ----  --------  ---------  ------  ----------     ------
Totals:        160         130    81.3         129       80.6
--------------------------------------------------------------
```

```
File Name:  cd-10
Statistical Analysis File (.STT)


----------------------------------------
 *** Summary Performance Statistics ***
----------------------------------------
Analyte:  Cd          Matrix:  Acid Mine Drainage
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

------------------------------------------------------------------------------------------------------------------------
            LEVEL:         1         2         3         4         5         6         7         8         9        10
------------------------------------------------------------------------------------------------------------------------
YOUDEN PAIRS:         Pair 1    Pair 1    Pair 2    Pair 2    Pair 3    Pair 3    Pair 4    Pair 4    Pair 5    Pair 5
                       (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)
------------------------------------------------------------------------------------------------------------------------
CONCENTRATION:        3.5385    3.5385   19.5385   28.0385   39.8385   47.9385   62.2385   70.9385   84.7385   92.8385
------------------------------------------------------------------------------------------------------------------------
RECOVERY:
 Observations             13        13        13        13        13        13        13        13        12        13
 Mean Result          3.6077    3.4692   22.5154   30.1077   42.4154   51.6923   66.9000   75.2385   86.6750   96.6077
 Bias                  .0692    -.0693    2.9769    2.0692    2.5769    3.7538    4.6615    4.3000    1.9365    3.7692
 Relative Bias %      1.9554   -1.9576   15.2360    7.3798    6.4683    7.8305    7.4897    6.0615    2.2853    4.0599
 Maximum Result       6.0000    7.0000   30.0000   45.7000   60.0000   73.0000   87.0000   94.0000  106.0000  122.0000
 Minimum Result        .0000     .0000   18.0000   15.6000   22.2000   37.8000   44.4000   55.3000   66.7000   73.0000
------------------------------------------------------------------------------------------------------------------------
SINGLE OPERATOR PRECISION:   Pair 1              Pair 2              Pair 3              Pair 4              Pair 5
   Observations                  13                  13                  13                  13                  12
   Standard Deviation         .4818              4.8117              2.7939              3.2560              7.5410
   Correction Factor         1.0210              1.0210              1.0210              1.0210              1.0230
   Corrected Std Dev          .4919              4.9128              2.8527              3.3244              7.7141
   Relative Std Dev (%)     13.9019             18.6718              6.0626              4.6777              8.3996
------------------------------------------------------------------------------------------------------------------------
OVERALL PRECISION:
 Observations              13        13        13        13        13        13        13        13        12        13
 Standard Deviation    1.4947    1.6183    3.2580    7.1059    8.7599    9.3963   11.7527   11.4969   10.6467   14.6376
 Correction Factor     1.0210    1.0210    1.0210    1.0210    1.0210    1.0210    1.0210    1.0210    1.0230    1.0210
 Corrected Std Dev     1.5261    1.6524    3.3265    7.2553    8.9441    9.5939   11.9998   11.7386   10.8911   14.9454
 Relative Std Dev %   42.3018   47.6288   14.7745   24.0980   21.0870   18.5596   17.9369   15.6019   12.5654   15.4702
------------------------------------------------------------------------------------------------------------------------
```

```
File Name:  cd-10
Statistical Analysis File (.STT)


----------------------------------
  *** Results of Bias Testing ***
----------------------------------
 Analyte:  Cd          Matrix:  Acid Mine Drainage
 Project:  AMQ-TC      Method:  GFAAS
    Date:  12/13/1995
   Units:  ug/L

------------------------------------------------------------------------
                                    Rel.    Obs     Crit   Statistically
Conc.             Mean              Bias      t        t     Significant
Level   Conc    Result      Bias     (%)  Value    Value   (1% Two-Tail)
------------------------------------------------------------------------
 1    3.5385    3.6077     .0692    1.96   .166    3.055         NO
 2    3.5385    3.4692    -.0693   -1.96   .154    3.055         NO
 3   19.5385   22.5154    2.9769   15.24  3.294    3.055        YES
 4   28.0385   30.1077    2.0692    7.38  1.050    3.055         NO
 5   39.8385   42.4154    2.5769    6.47  1.061    3.055         NO
 6   47.9385   51.6923    3.7538    7.83  1.440    3.055         NO
 7   62.2385   66.9000    4.6615    7.49  1.430    3.055         NO
 8   70.9385   75.2385    4.3000    6.06  1.349    3.055         NO
 9   84.7385   86.6750    1.9365    2.29   .630    3.106         NO
10   92.8385   96.6077    3.7692    4.06   .928    3.055         NO
------------------------------------------------------------------------
```

```
File Name:  cd-10
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***   Single Operator Precision    ***
----------------------------------------
Analyte:  Cd          Matrix:  Acid Mine Drainage
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):      .6454
          Slope (b):      .0745
    =============================
                                           Single
           Sample Weights                Operator   Estimated
    Pair   Size       (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      13     65.79      3.5385       .4919       .9092
      2      13     18.39     23.7885      4.9128      2.4185
      3      13      8.54     43.8885      2.8527      3.9167
      4      13      4.62     66.5885      3.3244      5.6087
      5      12      2.67     88.7885      7.7141      7.2634
    -----------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    =========================================================
      a:      .9581      Intercept (a'):     -.0428
      b:     1.0241          Slope (b'):      .0238
    =========================================================
                                                  Single
           Sample Weight                Operator   Estimated
    Pair   Size      (%)        Conc     Std Dev     Std Dev
    ---------------------------------------------------------
      1      13    20.35      3.5385       .4919      1.0423
      2      13    20.35      3.5385      4.9128      1.6874
      3      13    20.35     19.5385      2.8527      2.7222
      4      13    20.35     28.0385      3.3244      4.6717
      5      12    18.62     39.8385      7.7141      7.9225
    ---------------------------------------------------------
```

```
File Name:  cd-10
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***       Overall Precision        ***
----------------------------------------
Analyte:  Cd          Matrix:  Acid Mine Drainage
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Overall Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):     1.0781
          Slope (b):      .1615
    =============================
    Conc   Sample   Weights                 Overall   Estimated
    Level  Size         (%)        Conc     Std Dev     Std Dev
    -------------------------------------------------------------
      1      13       36.07      3.5385      1.5261      1.6495
      2      13       36.07      3.5385      1.6524      1.6495
      3      13        9.74     19.5385      3.3265      4.2336
      4      13        6.18     28.0385      7.2553      5.6064
      5      13        3.76     39.8385      8.9441      7.5121
      6      13        2.84     47.9385      9.5939      8.8202
      7      13        1.87     62.2385     11.9998     11.1297
      8      13        1.51     70.9385     11.7386     12.5348
      9      12        1.02     84.7385     10.8911     14.7635
     10      13         .95     92.8385     14.9454     16.0717
    -------------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    ===========================================================
      a:     2.2015      Intercept (a'):      .7891
      b:     1.0240          Slope (b'):      .0237
    ===========================================================
    Conc   Sample   Weight                 Overall   Estimated
    Level  Size        (%)       Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      13      10.09      3.5385      1.5261      2.3942
      2      13      10.09      3.5385      1.6524      2.3942
      3      13      10.09     19.5385      3.3265      3.4986
      4      13      10.09     28.0385      7.2553      4.2797
      5      13      10.09     39.8385      8.9441      5.6613
      6      13      10.09     47.9385      9.5939      6.8598
      7      13      10.09     62.2385     11.9998      9.6283
      8      13      10.09     70.9385     11.7386     11.8339
      9      12       9.23     84.7385     10.8911     16.4141
     10      13      10.09     92.8385     14.9454     19.8892
    -----------------------------------------------------------
```

```
File Name:  cd-10
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ************  Recovery  **************
----------------------------------------
Analyte:  Cd          Matrix:  Acid Mine Drainage
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Recovery ***

    - Linear Model - X = b*T + a
    =============================
      Intercept (a):     -.1210
          Slope (b):     1.0686
    =============================
    Conc   Sample   Weights                  Mean   Estimated
    Level  Size         (%)      Conc      Result      Result
    ----------------------------------------------------------
      1      13     41.97      3.5385      3.6077      3.6601
      2      13     41.97      3.5385      3.4692      3.6601
      3      13      6.37     19.5385     22.5154     20.7572
      4      13      3.63     28.0385     30.1077     29.8400
      5      13      2.02     39.8385     42.4154     42.4490
      6      13      1.47     47.9385     51.6923     51.1044
      7      13       .92     62.2385     66.9000     66.3849
      8      13       .73     70.9385     75.2385     75.6814
      9      12       .48     84.7385     86.6750     90.4276
     10      13       .44     92.8385     96.6077     99.0830
    ----------------------------------------------------------


File Name:  cd-10
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***     Precision vs Recovery      ***
----------------------------------------
Analyte:  Cd          Matrix:  Acid Mine Drainage
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision vs Recovery ***
          (Obtained by Substitution)

     - Linear Model - s = f*X + e
    ==============================
        Intercept (e):      .7586
            Slope (f):      .0698
    ==============================


     - Curvilinear Model - s = e*(f**X)
    ====================================
        Intercept (e):      .9607
                  (f):     1.0225
    ====================================



 *** Overall Precision vs Recovery ***
      (Obtained by Substitution)

     - Linear Model - s = f*X + e
     =============================
        Intercept (e):     1.1913
            Slope (f):      .1511
     =============================


     - Curvilinear Model - s = e*(f**X)
     ===================================
        Intercept (e):     2.2074
                  (f):     1.0224
     ===================================
```

```
cr-5.dat

Cr     5   1     0.0000   -0.0200    6.1100    8.5100   15.3000   21.1000   49.9000   56.9000   84.8000  101.8000
Cr     5   2    -0.2000   -0.3000    5.1000    8.4000   15.4000   21.3000   38.3000   42.4000   65.6000   80.6000
Cr     5   5     0.5000    0.2000    5.3000    8.7000   15.2000   21.5000   47.1000   55.2000   85.3000  101.3000
Cr     5   6    -0.7000   -0.9000    4.3000    7.6000   15.4000   22.0000   49.2000   55.0000   85.9000   96.3000
Cr     5   7    -0.4930   -0.6500    6.0800    8.1400   16.1000   23.2000   49.8000   56.1000   81.9000   92.6000
Cr     5   8     2.5000   -1.2000    5.0000   10.1000   13.3000   22.0000   50.2000   46.1000   84.1000   89.9000
Cr     5  10     0.7000    0.8000    6.1000    7.5000   15.7000   22.3000   45.1000   57.1000   82.7000   87.0000
Cr     5  11    -0.1000   -0.1000    5.6000    8.1000   15.8000   21.9000   47.2000   53.7000   84.7000   88.2000
Cr     5  15     0.6000    1.1000    5.9000    8.5000   16.2000   22.0000   49.9000   51.6000   82.7000   80.6000
Cr     5  16     2.2000    7.8000   10.6000   11.1000   22.8000   28.3000   36.7000   67.8000   67.8000   88.3000
Cr     5  17     1.0000    0.0000    6.0000    9.0000   16.0000   23.0000   52.0000   59.0000   89.0000  119.7000
Cr     5  20     1.5000    0.7000    5.1000    7.2000   16.8000   22.7000   45.0000   52.6000   81.2000   90.4000
Cr     5  21     4.8000    0.1000    6.8000   10.0000   17.4000   22.9000   48.7000   54.1000   80.0000   95.7000
Cr     5  24     0.0000    0.9800    5.5000   11.1000   19.8000   29.2000   70.5000   66.3000   62.8000   97.6000
Cr     5  25     0.3000    0.0000    7.1000    8.4000   18.6000   18.4000   41.6000   57.6000   88.0000   92.4000
Cr     5  26     0.2000    0.2000    5.8000    8.1000   15.8000   21.8000   49.2000   56.0000   86.0000   99.0000
Cr     5  27     0.0000    1.0000    6.0000   10.0000   15.0000   16.0000   43.0000   45.0000   88.0000   78.0000
```

```
File Name:  cr-5
Data Validation File (.DA~)

******************************************************************************
***                   Parameter and Data Validation File                   ***
******************************************************************************
   Analyte:  Cr              Matrix:  Reagent Grade Water
   Project:  AMQ-TC       Matrix ID:   5
      Date:  12/13/1995      Method:  GFAAS
     Pairs:  5
     Units:  ug/L

---------------------------------------------------------------------------------------------------------------------------------
Level          1          2            3          4            5          6            7          8            9         10
---------------------------------------------------------------------------------------------------------------------------------
Spike          .3472      .0000       5.2000     2.7000       7.1000     6.1000      24.4000     6.4000      27.4000    11.8000
Spike
Increment      .0000      .0000       5.2000     7.9000      15.0000    21.1000      45.5000    51.9000      79.3000    91.1000
---------------------------------------------------------------------------------------------------------------------------------

                 Final Concentration
         ------------------------------------------------------------------------------------------------------------------------
Lab ID         .3472      .3472       5.5472     8.2472      15.3472    21.4472      45.8472    52.2472      79.6472    91.4472
---------------------------------------------------------------------------------------------------------------------------------
    1          .0000     -.0200       6.1100     8.5100      15.3000    21.1000      49.9000    56.9000      84.8000   101.8000
    2    r    -.2000r    -.3000  r    5.1000r    8.4000  r   15.4000r   21.3000  r   38.3000r   42.4000  r   65.6000r   80.6000
    5          .5000      .2000       5.3000     8.7000      15.2000    21.5000      47.1000    55.2000      85.3000   101.3000
    6         -.7000     -.9000       4.3000     7.6000      15.4000    22.0000      49.2000    55.0000      85.9000    96.3000
    7         -.4930     -.6500       6.0800     8.1400      16.1000    23.2000      49.8000    56.1000      81.9000    92.6000
    8         2.5000    -1.2000       5.0000    10.1000      13.3000    22.0000      50.2000    46.1000      84.1000    89.9000
   10          .7000      .8000       6.1000     7.5000      15.7000    22.3000      45.1000    57.1000      82.7000    87.0000
   11         -.1000     -.1000       5.6000     8.1000      15.8000    21.9000      47.2000    53.7000      84.7000    88.2000
   15          .6000     1.1000       5.9000     8.5000      16.2000    22.0000      49.9000    51.6000      82.7000    80.6000
   16         2.2000o    7.8000  o   10.6000    11.1000  o   22.8000    28.3000      36.7000    67.8000  ?   67.8000    88.3000
   17         1.0000      .0000       6.0000     9.0000      16.0000    23.0000      52.0000    59.0000      89.0000o  119.7000
   20         1.5000      .7000       5.1000     7.2000      16.8000    22.7000      45.0000    52.6000      81.2000    90.4000
   21    o    4.8000      .1000       6.8000    10.0000      17.4000    22.9000      48.7000    54.1000      80.0000    95.7000
   24          .0000      .9800       5.5000    11.1000      19.8000    29.2000  o   70.5000    66.3000  o   62.8000    97.6000
   25          .3000      .0000       7.1000     8.4000      18.6000    18.4000      41.6000    57.6000      88.0000    92.4000
   26          .2000      .2000       5.8000     8.1000      15.8000    21.8000      49.2000    56.0000      86.0000    99.0000
   27          .0000     1.0000       6.0000    10.0000      15.0000    16.0000      43.0000    45.0000      88.0000    78.0000
---------------------------------------------------------------------------------------------------------------------------------
```

```
cr-5.daf

Cr     5   1      .0000    -.0200    6.1100    8.5100   15.3000   21.1000   49.9000   56.9000   84.8000  101.8000
Cr     5   5      .5000     .2000    5.3000    8.7000   15.2000   21.5000   47.1000   55.2000   85.3000  101.3000
Cr     5   6     -.7000    -.9000    4.3000    7.6000   15.4000   22.0000   49.2000   55.0000   85.9000   96.3000
Cr     5   7     -.4930    -.6500    6.0800    8.1400   16.1000   23.2000   49.8000   56.1000   81.9000   92.6000
Cr     5   8     2.5000   -1.2000    5.0000   10.1000   13.3000   22.0000   50.2000   46.1000   84.1000   89.9000
Cr     5  10      .7000     .8000    6.1000    7.5000   15.7000   22.3000   45.1000   57.1000   82.7000   87.0000
Cr     5  11     -.1000    -.1000    5.6000    8.1000   15.8000   21.9000   47.2000   53.7000   84.7000   88.2000
Cr     5  15      .6000    1.1000    5.9000    8.5000   16.2000   22.0000   49.9000   51.6000   82.7000   80.6000
Cr     5  16     2.2000o         o              11.1000o            28.3000   36.7000   67.8000   67.8000   88.3000
Cr     5  17     1.0000     .0000    6.0000    9.0000   16.0000   23.0000   52.0000   59.0000   89.0000o
Cr     5  20     1.5000     .7000    5.1000    7.2000   16.8000   22.7000   45.0000   52.6000   81.2000   90.4000
Cr     5  21 o              .1000    6.8000   10.0000   17.4000   22.9000   48.7000   54.1000   80.0000   95.7000
Cr     5  24      .0000     .9800    5.5000   11.1000   19.8000   29.2000o            66.3000o            97.6000
Cr     5  25      .3000     .0000    7.1000    8.4000   18.6000   18.4000   41.6000   57.6000   88.0000   92.4000
Cr     5  26      .2000     .2000    5.8000    8.1000   15.8000   21.8000   49.2000   56.0000   86.0000   99.0000
Cr     5  27      .0000    1.0000    6.0000   10.0000   15.0000   16.0000   43.0000   45.0000   88.0000   78.0000
```

```
File Name:  cr-5
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Reagent Grade Water
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
------------------------------------------------------------
 ***        Results of 5x - 1/5x Mean Error Check       ***
 ***         Questionable Data (Positive Values)        ***
------------------------------------------------------------
 Conc  Lab  Rep     Mean
 Lev   No   No     Result     Result                   Ratio
------------------------------------------------------------
  1     21  1       .8412     4.8000                  5.71
  2     16  1       .7576     7.8000                 10.30
  2     21  1       .7576      .1000                   .13
------------------------------------------------------------
Total Number of Questionable Observations:     3


------------------------------------------------------------
 ***        Results of Factor of 5 Error Check          ***
 ***          Questionable Data (All Values)            ***
------------------------------------------------------------
 Conc  Lab  Rep     Mean                  Mean   Obs
 Lev   No   No     Result     Result     Dev    Dev   Ratio
------------------------------------------------------------
  2    16   1       .5712     7.8000    1.053    7.229  6.86
  3    16   1      6.0229    10.6000     .783    4.577  5.85
------------------------------------------------------------
Total Number of Questionable Observations:     2
```

```
File Name:  cr-5
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Reagent Grade Water
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
---------------------------------------------
 ***      Laboratory Ranking Results      ***
 ***   Two-Tailed 5% Significance Level   ***
 ***--------------------------------------***
 ***     Upper Critical Value:    135.0   ***
 ***     Lower Critical Value:     45.0   ***
---------------------------------------------

      Ranks
     ----------------------------------------------------------------------------
       Rank  Level  Level  Level  Level  Level  Level  Level  Level  Level  Level
Lab    Sums    1      2      3      4      5      6      7      8      9     10
---- ----------------------------------------------------------------------------
  1    95.5   6.00   6.00  14.00  10.00   4.00   3.00  13.50  12.00  11.00  16.00
  2    35.0   3.00   4.00   3.50   7.50   5.50   4.00   2.00   1.00   2.00   2.50
  5    87.5  10.00  10.50   5.00  11.00   3.00   5.00   7.00   9.00  12.00  15.00
  6    65.0   1.00   2.00   1.00   3.00   5.50   9.00  10.50   8.00  13.00  12.00
  7    88.0   2.00   3.00  12.00   6.00  11.00  15.00  12.00  11.00   6.00  10.00
  8    78.0  16.00   1.00   2.00  15.00   1.00   9.00  15.00   3.00   9.00   7.00
 10    88.5  12.00  13.00  13.00   2.00   7.00  11.00   6.00  13.00   7.50   4.00
 11    65.0   4.00   5.00   7.00   4.50   8.50   7.00   8.00   6.00  10.00   5.00
 15    93.5  11.00  16.00   9.00   9.00  12.00   9.00  13.50   4.00   7.50   2.50
 16   125.5  15.00  17.00  17.00  16.50  17.00  16.00   1.00  17.00   3.00   6.00
 17   132.0  13.00   7.50  10.50  12.00  10.00  14.00  16.00  15.00  17.00  17.00
 20    78.5  14.00  12.00   3.50   1.00  13.00  12.00   5.00   5.00   5.00   8.00
 21   112.5  17.00   9.00  15.00  13.50  14.00  13.00   9.00   7.00   4.00  11.00
 24   122.5   6.00  14.00   6.00  16.50  16.00  17.00  17.00  16.00   1.00  13.00
 25    98.5   9.00   7.50  16.00   7.50  15.00   2.00   3.00  14.00  15.50   9.00
 26    94.0   8.00  10.50   8.00   4.50   8.50   6.00  10.50  10.00  14.00  14.00
 27    70.5   6.00  15.00  10.50  13.50   2.00   1.00   4.00   2.00  15.50   1.00
-------------------------------------------------
 *** Laboratory   2 Rejected; Rank Sum   35.0 ***
-------------------------------------------------
```

```
File Name:  cr-5
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Reagent Grade Water
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
----------------------------------------
 ***    Outlier Testing Results      ***
 *** Two-Sided 5% Significance Level ***
----------------------------------------

--------------------
   - Outlier(s) -
--------------------
 Lev  Iter  Lab  Rep     Result      Mean    Std Dev    t     Crit t   n
---------------------------------------------------------------------------
  1     1    21   1      4.8000      .8129     1.3851   2.878   2.585   16
  2     1    16   1      7.8000      .6256     2.0273   3.539   2.585   16
  3     1    16   1     10.6000     6.0806     1.3804   3.274   2.585   16
  5     1    16   1     22.8000    16.5750     2.2323   2.789   2.585   16
  7     1    24   1     70.5000    48.4437     7.0724   3.119   2.585   16
  9     1    24   1     62.8000    82.1813     7.1088   2.726   2.585   16
  *     1    17   1    119.7000    93.6750     9.6749   2.690   2.585   16
---------------------------------------------------------------------------
```

```
File Name:  cr-5
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Reagent Grade Water
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------
 *** Results of Normality Testing ***
-------------------------------------------

-------------------------
   - Normality Tests -
-------------------------
               Test  Normality      Test          Critical
   Level  n    Type  Accept/Reject  Statistic     Value(s)
---------------------------------------------------------------
     1    15     W     A              .9132      .881   ---
     2    15     W     A              .9352      .881   ---
     3    15     W     A              .9653      .881   ---
     4    16     W     A              .9124      .887   ---
     5    15     W     A              .9120      .881   ---
     6    16     W            R       .8478      .887   ---
     7    15     W            R       .8803      .881   ---
     8    16     W     A              .9302      .887   ---
     9    15     W            R       .7824      .881   ---
    10    15     W     A              .9576      .881   ---
-------------------------------
 - 3 Normality Rejection(s) -
-------------------------------
```

```
File Name:  cr-5
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Reagent Grade Water
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------------
 ***         Data Removal Tracking         ***
 *** Simple Count of Remaining Data Points ***
 ***          After Removal Tests          ***
-----------------------------------------------

             Points   After Lab Ranking  After Outlier Testing
               As     -----------------  ---------------------
 Lev  Mtrx  Received     Points    %         Points       %

 ---  ----  --------  ---------  ------  ----------     ------
  1     5       17           16    94.1          15       88.2
  2     5       17           16    94.1          15       88.2
  3     5       17           16    94.1          15       88.2
  4     5       17           16    94.1          16       94.1
  5     5       17           16    94.1          15       88.2
  6     5       17           16    94.1          16       94.1
  7     5       17           16    94.1          15       88.2
  8     5       17           16    94.1          16       94.1
  9     5       17           16    94.1          15       88.2
 10     5       17           16    94.1          15       88.2
 ---  ----  --------  ---------  ------  ----------     ------
Totals:        170          160    94.1         153       90.0
--------------------------------------------------------------
```

```
File Name:  cr-5
Statistical Analysis File (.STT)


----------------------------------------
 *** Summary Performance Statistics ***
----------------------------------------
Analyte:  Cr          Matrix:  Reagent Grade Water
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

------------------------------------------------------------------------------------------------------------------------
            LEVEL:         1         2         3         4         5         6         7         8         9        10
------------------------------------------------------------------------------------------------------------------------
YOUDEN PAIRS:         Pair 1    Pair 1    Pair 2    Pair 2    Pair 3    Pair 3    Pair 4    Pair 4    Pair 5    Pair 5
                       (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)
------------------------------------------------------------------------------------------------------------------------
CONCENTRATION:         .3472     .3472    5.5472    8.2472   15.3472   21.4472   45.8472   52.2472   79.6472   91.4472
------------------------------------------------------------------------------------------------------------------------
RECOVERY:
 Observations             15        15        15        16        15        16        15        16        15        15
 Mean Result           .5471     .1473    5.7793    8.8781   16.1600   22.3937   46.9733   55.6312   83.4733   91.9400
 Bias                  .1999    -.1999     .2321     .6309     .8128     .9465    1.1261    3.3840    3.8261     .4928
 Relative Bias %     57.5845  -57.5653    4.1847    7.6502    5.2961    4.4134    2.4563    6.4770    4.8039     .5389
 Maximum Result       2.5000    1.1000    7.1000   11.1000   19.8000   29.2000   52.0000   67.8000   89.0000  101.8000
 Minimum Result       -.7000   -1.2000    4.3000    7.2000   13.3000   16.0000   36.7000   45.0000   67.8000   78.0000
------------------------------------------------------------------------------------------------------------------------
SINGLE OPERATOR PRECISION:   Pair 1              Pair 2              Pair 3              Pair 4              Pair 5
   Observations                  14                  15                  15                  15                  14
   Standard Deviation         .8017               .8625              1.7452              5.5292              5.8007
   Correction Factor         1.0194              1.0180              1.0180              1.0180              1.0194
   Corrected Std Dev          .8172               .8780              1.7766              5.6287              5.9132
   Relative Std Dev (%)    235.3601             11.8988              9.1683             10.9419              6.7421
------------------------------------------------------------------------------------------------------------------------
OVERALL PRECISION:
 Observations              15        15        15        16        15        16        15        16        15        15
 Standard Deviation     .9190     .6942     .6968    1.2259    1.5449    3.0871    4.0653    5.8721    5.0521    6.9774
 Correction Factor     1.0180    1.0180    1.0180    1.0168    1.0180    1.0168    1.0180    1.0168    1.0180    1.0180
 Corrected Std Dev      .9355     .7067     .7094    1.2465    1.5727    3.1389    4.1385    5.9707    5.1430    7.1030
 Relative Std Dev %  170.9820  479.6907   12.2745   14.0398    9.7323   14.0169    8.8103   10.7326    6.1613    7.7257
------------------------------------------------------------------------------------------------------------------------
```

```
File Name:  cr-5
Statistical Analysis File (.STT)


----------------------------------
  *** Results of Bias Testing ***
----------------------------------
 Analyte:  Cr          Matrix:  Reagent Grade Water
 Project:  AMQ-TC      Method:  GFAAS
    Date:  12/13/1995
   Units:  ug/L

------------------------------------------------------------------------
                                    Rel.    Obs     Crit   Statistically
Conc.             Mean              Bias      t        t     Significant
Level   Conc    Result      Bias     (%)   Value   Value   (1% Two-Tail)
------------------------------------------------------------------------
 1     .3472     .5471     .1999   57.58    .841   2.977         NO
 2     .3472     .1473    -.1999  -57.57   1.115   2.977         NO
 3    5.5472    5.7793     .2321    4.18   1.290   2.977         NO
 4    8.2472    8.8781     .6309    7.65   2.059   2.947         NO
 5   15.3472   16.1600     .8128    5.30   2.038   2.977         NO
 6   21.4472   22.3937     .9465    4.41   1.226   2.947         NO
 7   45.8472   46.9733    1.1261    2.46   1.073   2.977         NO
 8   52.2472   55.6312    3.3840    6.48   2.305   2.947         NO
 9   79.6472   83.4733    3.8261    4.80   2.933   2.977         NO
10   91.4472   91.9400     .4928     .54    .274   2.977         NO
------------------------------------------------------------------------
```

```
File Name:  cr-5
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***   Single Operator Precision    ***
----------------------------------------
Analyte:  Cr          Matrix:  Reagent Grade Water
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):      .6649
          Slope (b):      .0729
    =============================
                                           Single
           Sample Weights                Operator   Estimated
    Pair   Size       (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      14     59.43       .3472       .8172       .6902
      2      15     26.88      6.8972       .8780      1.1677
      3      15     10.26     18.3972      1.7766      2.0061
      4      15      2.52     49.0472      5.6287      4.2405
      5      14       .91     85.5472      5.9132      6.9014
    -----------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    =========================================================
      a:      .9387      Intercept (a'):     -.0632
      b:     1.0259          Slope (b'):      .0256
    =========================================================
                                                  Single
           Sample Weight                Operator   Estimated
    Pair   Size      (%)        Conc     Std Dev     Std Dev
    ---------------------------------------------------------
      1      14    19.10       .3472       .8172       .9471
      2      15    20.60       .3472       .8780      1.1199
      3      15    20.60      5.5472      1.7766      1.5031
      4      15    20.60      8.2472      5.6287      3.2928
      5      14    19.10     15.3472      5.9132      8.3784
    ---------------------------------------------------------

File Name:  cr-5
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***       Overall Precision        ***
----------------------------------------
Analyte:  Cr          Matrix:  Reagent Grade Water
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Overall Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):      .7091
          Slope (b):      .0755
    =============================
    Conc   Sample   Weights                 Overall   Estimated
    Level  Size         (%)        Conc     Std Dev     Std Dev
    -------------------------------------------------------------
      1      15       28.82       .3472       .9355       .7353
      2      15       28.82       .3472       .7067       .7353
      3      15       15.01      5.5472       .7094      1.1279
      4      16       12.29      8.2472      1.2465      1.3317
      5      15        6.46     15.3472      1.5727      1.8678
      6      16        4.70     21.4472      3.1389      2.3283
      7      15        1.51     45.8472      4.1385      4.1705
      8      16        1.31     52.2472      5.9707      4.6537
      9      15         .61     79.6472      5.1430      6.7224
     10      15         .48     91.4472      7.1030      7.6133
    -------------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    ===========================================================
      a:     1.0060      Intercept (a'):      .0060
      b:     1.0249          Slope (b'):      .0246
    ===========================================================
    Conc   Sample   Weight                 Overall   Estimated
    Level  Size        (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      15        9.79       .3472       .9355      1.0146
      2      15        9.79       .3472       .7067      1.0146
      3      15        9.79      5.5472       .7094      1.1531
      4      16       10.50      8.2472      1.2465      1.2324
      5      15        9.79     15.3472      1.5727      1.4676
      6      16       10.50     21.4472      3.1389      1.7054
      7      15        9.79     45.8472      4.1385      3.1088
      8      16       10.50     52.2472      5.9707      3.6391
      9      15        9.79     79.6472      5.1430      7.1422
     10      15        9.79     91.4472      7.1030      9.5487
    -----------------------------------------------------------
```

```
File Name:  cr-5
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ************  Recovery  **************
----------------------------------------
Analyte:  Cr          Matrix:  Reagent Grade Water
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Recovery ***

    - Linear Model - X = b*T + a
    =============================
      Intercept (a):      .0386
          Slope (b):     1.0391
    =============================
    Conc   Sample   Weights                  Mean   Estimated
    Level  Size         (%)      Conc      Result      Result
    ----------------------------------------------------------
      1      15     32.36       .3472       .5471       .3993
      2      15     32.36       .3472       .1473       .3993
      3      15     13.75      5.5472      5.7793      5.8026
      4      16     10.52      8.2472      8.8781      8.6081
      5      15      5.01     15.3472     16.1600     15.9855
      6      16      3.44     21.4472     22.3937     22.3239
      7      15      1.01     45.8472     46.9733     47.6775
      8      16       .86     52.2472     55.6312     54.3276
      9      15       .39     79.6472     83.4733     82.7984
     10      15       .30     91.4472     91.9400     95.0595
    ----------------------------------------------------------
```

```
File Name:  cr-5
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***     Precision vs Recovery      ***
----------------------------------------
Analyte:  Cr          Matrix:  Reagent Grade Water
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision vs Recovery ***
          (Obtained by Substitution)

     - Linear Model - s = f*X + e
    ==============================
        Intercept (e):      .6278
            Slope (f):      .0702
    ==============================


     - Curvilinear Model - s = e*(f**X)
    ====================================
        Intercept (e):      .9378
                  (f):     1.0249
    ====================================



 *** Overall Precision vs Recovery ***
      (Obtained by Substitution)

     - Linear Model - s = f*X + e
     =============================
        Intercept (e):      .6719
            Slope (f):      .0727
     =============================


     - Curvilinear Model - s = e*(f**X)
     ===================================
        Intercept (e):     1.0051
                  (f):     1.0240
     ===================================
```

```
cr-8.dat

Cr     8   1     0.0900    0.1300    8.4800    6.0500   14.8000   21.6000   42.5000   45.9000   83.5000   92.2000
Cr     8   2    -0.1000   -0.5000    4.4000    7.5000   17.6000   21.5000   45.1000   48.0000   97.0000  106.0000
Cr     8   5     0.6000    0.5000    4.7000    7.4000   19.5000   22.7000   50.3000   58.9000   80.9000   93.3000
Cr     8   6    -0.1000    1.6000    3.3000    6.4000   15.4000   19.1000   44.3000   49.6000   75.9000   90.7000
Cr     8   7     0.1410   -0.4470    4.4700    8.7400   20.4000   26.8000   55.4000   64.8000   86.2000  110.0000
Cr     8   8     0.0000    1.4000    5.4000    9.4000   23.4000   23.1000   57.6000   56.9000  103.0000  109.0000
Cr     8  10     0.8000    1.0000    3.9000    6.1000   15.9000   21.3000   53.1000   59.1000   78.5000   84.9000
Cr     8  11     0.2000   -0.1000    4.9000    8.3000   20.0000   25.1000   54.7000   64.3000   86.1000  104.0000
Cr     8  15     1.1000    0.9000    4.4000    7.5000   18.1000   23.3000   48.2000   54.1000   92.3000   98.9000
Cr     8  16     7.2000    6.1000   11.1000   16.7000   32.8000   38.9000   75.6000   90.0000  125.6000  143.9000
Cr     8  17     6.0000    5.0000    5.0000    9.0000   28.0000   28.0000   75.0000   70.0000  100.0000   30.0000
Cr     8  20     1.0000    0.6000  266.0000   10.1000   20.5000   25.7000   54.1000   67.6000   90.7000   96.4000
Cr     8  21     4.1000    2.1000    7.1000    8.6000   18.7000   25.6000   50.6000   59.7000   82.2000   97.4000
Cr     8  24     0.2700    0.0000    4.0100   11.7000   29.1000   31.3000   54.5000   83.8000   87.2000   87.6000
Cr     8  25     0.4000    0.0000    5.0000    8.9000   21.8000   16.8000   49.6000   51.7000   77.7000  101.2000
Cr     8  26     0.0000   -0.1000    5.0000    7.7000   19.3000   23.8000   53.0000   73.5000   92.0000  103.0000
Cr     8  27    -1.0000    0.0000    6.0000    9.0000   20.0000   24.0000   48.0000   64.0000   86.0000   99.0000
```

```
File Name:  cr-8
Data Validation File (.DA~)

******************************************************************************
***                   Parameter and Data Validation File                   ***
******************************************************************************
   Analyte:  Cr             Matrix:  Freshwater
   Project:  AMQ-TC       Matrix ID:   8
      Date:  12/13/1995      Method:  GFAAS
     Pairs:  5
     Units:  ug/L

---------------------------------------------------------------------------------------------------------------------------------
Level          1          2            3          4            5          6            7          8            9         10
---------------------------------------------------------------------------------------------------------------------------------
Spike          .4673      .0000      4.8000      3.0000      11.7000     5.0000      30.0000     8.0000      24.7000    12.5000
Spike
Increment      .0000      .0000      4.8000      7.8000      19.5000    24.5000      54.5000    62.5000      87.2000    99.7000
---------------------------------------------------------------------------------------------------------------------------------

                 Final Concentration
         ------------------------------------------------------------------------------------------------------------------------
Lab ID         .4673      .4673      5.2673      8.2673      19.9673    24.9673      54.9673    62.9673      87.6673   100.1673
---------------------------------------------------------------------------------------------------------------------------------
    1          .0900      .1300  ?   8.4800      6.0500      14.8000    21.6000      42.5000    45.9000      83.5000    92.2000
    2         -.1000     -.5000      4.4000      7.5000      17.6000    21.5000      45.1000    48.0000      97.0000   106.0000
    5          .6000      .5000      4.7000      7.4000      19.5000    22.7000      50.3000    58.9000      80.9000    93.3000
    6    r    -.1000r    1.6000  r   3.3000r     6.4000  r   15.4000r   19.1000  r   44.3000r   49.6000  r   75.9000r   90.7000
    7          .1410     -.4470      4.4700      8.7400      20.4000    26.8000      55.4000    64.8000      86.2000   110.0000
    8          .0000     1.4000      5.4000      9.4000      23.4000    23.1000      57.6000    56.9000     103.0000   109.0000
   10          .8000     1.0000      3.9000      6.1000      15.9000    21.3000      53.1000    59.1000      78.5000    84.9000
   11          .2000     -.1000      4.9000      8.3000      20.0000    25.1000      54.7000    64.3000      86.1000   104.0000
   15         1.1000      .9000      4.4000      7.5000      18.1000    23.3000      48.2000    54.1000      92.3000    98.9000
   16    r    7.2000r    6.1000  r  11.1000r    16.7000  r   32.8000r   38.9000  r   75.6000r   90.0000  r  125.6000r  143.9000
   17    o    6.0000o    5.0000      5.0000      9.0000      28.0000    28.0000  o   75.0000    70.0000     100.0000o   30.0000
   20         1.0000      .6000  o 266.0000     10.1000      20.5000    25.7000      54.1000    67.6000      90.7000    96.4000
   21    ?    4.1000     2.1000      7.1000      8.6000      18.7000    25.6000      50.6000    59.7000      82.2000    97.4000
   24          .2700      .0000      4.0100     11.7000      29.1000    31.3000      54.5000    83.8000      87.2000    87.6000
   25          .4000      .0000      5.0000      8.9000      21.8000    16.8000      49.6000    51.7000      77.7000   101.2000
   26          .0000     -.1000      5.0000      7.7000      19.3000    23.8000      53.0000    73.5000      92.0000   103.0000
   27        -1.0000      .0000      6.0000      9.0000      20.0000    24.0000      48.0000    64.0000      86.0000    99.0000
---------------------------------------------------------------------------------------------------------------------------------
```

```
cr-8.daf

Cr     8   1      .0900     .1300    8.4800    6.0500   14.8000   21.6000   42.5000   45.9000   83.5000   92.2000
Cr     8   2     -.1000    -.5000    4.4000    7.5000   17.6000   21.5000   45.1000   48.0000   97.0000  106.0000
Cr     8   5      .6000     .5000    4.7000    7.4000   19.5000   22.7000   50.3000   58.9000   80.9000   93.3000
Cr     8   7      .1410    -.4470    4.4700    8.7400   20.4000   26.8000   55.4000   64.8000   86.2000  110.0000
Cr     8   8      .0000    1.4000    5.4000    9.4000   23.4000   23.1000   57.6000   56.9000  103.0000  109.0000
Cr     8  10      .8000    1.0000    3.9000    6.1000   15.9000   21.3000   53.1000   59.1000   78.5000   84.9000
Cr     8  11      .2000    -.1000    4.9000    8.3000   20.0000   25.1000   54.7000   64.3000   86.1000  104.0000
Cr     8  15     1.1000     .9000    4.4000    7.5000   18.1000   23.3000   48.2000   54.1000   92.3000   98.9000
Cr     8  17 o         o             5.0000    9.0000   28.0000   28.0000o            70.0000  100.0000o
Cr     8  20     1.0000     .6000o            10.1000   20.5000   25.7000   54.1000   67.6000   90.7000   96.4000
Cr     8  21     4.1000    2.1000    7.1000    8.6000   18.7000   25.6000   50.6000   59.7000   82.2000   97.4000
Cr     8  24      .2700     .0000    4.0100   11.7000   29.1000   31.3000   54.5000   83.8000   87.2000   87.6000
Cr     8  25      .4000     .0000    5.0000    8.9000   21.8000   16.8000   49.6000   51.7000   77.7000  101.2000
Cr     8  26      .0000    -.1000    5.0000    7.7000   19.3000   23.8000   53.0000   73.5000   92.0000  103.0000
Cr     8  27    -1.0000     .0000    6.0000    9.0000   20.0000   24.0000   48.0000   64.0000   86.0000   99.0000
```

```
File Name:  cr-8
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Freshwater
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------------------------
 ***        Results of 5x - 1/5x Mean Error Check        ***
 ***         Questionable Data (Positive Values)         ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean
 Lev   No   No     Result     Result                   Ratio
-------------------------------------------------------------
  1      1  1      1.2883      .0900                    .07
  1      7  1      1.2883      .1410                    .11
  1     11  1      1.2883      .2000                    .16
  1     16  1      1.2883     7.2000                   5.59
  2      1  1      1.1371      .1300                    .11
  2     16  1      1.1371     6.1000                   5.36
  3      6  1     20.7741     3.3000                    .16
  3     10  1     20.7741     3.9000                    .19
  3     20  1     20.7741   266.0000                  12.80
  3     24  1     20.7741     4.0100                    .19
-------------------------------------------------------------
Total Number of Questionable Observations:    10


-------------------------------------------------------------
 ***        Results of Factor of 5 Error Check           ***
 ***          Questionable Data (All Values)             ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean                 Mean    Obs
 Lev   No   No     Result     Result     Dev     Dev   Ratio
-------------------------------------------------------------
  3    20   1     20.7741   266.0000   28.850  245.226  8.50
  4    16   1      8.7700    16.7000    1.578    7.930  5.03
 10    17   1     96.9118    30.0000   12.151   66.912  5.51
-------------------------------------------------------------
Total Number of Questionable Observations:     3
```

```
File Name:  cr-8
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Freshwater
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------------
 ***      Laboratory Ranking Results       ***
 ***   Two-Tailed 5% Significance Level   ***
 ***---------------------------------------***
 ***     Upper Critical Value:    135.0   ***
 ***     Lower Critical Value:     45.0   ***
-----------------------------------------------

      Ranks
     -----------------------------------------------------------------------------
       Rank  Level  Level  Level  Level  Level  Level  Level  Level  Level  Level
Lab    Sums    1      2      3      4      5      6      7      8      9     10
---- -----------------------------------------------------------------------------
  1    49.0   6.00   8.00  15.00   1.00   1.00   5.00   1.00   1.00   6.00   5.00
  2    54.5   2.50   1.00   4.50   5.50   4.00   4.00   3.00   2.00  14.00  14.00
  5    69.0  11.00   9.00   7.00   4.00   8.00   6.00   7.00   7.00   4.00   6.00
  6    34.5   2.50  14.00   1.00   3.00   2.00   2.00   2.00   3.00   1.00   4.00
  7   101.0   7.00   2.00   6.00  10.00  11.00  14.00  14.00  12.00   9.00  16.00
  8   116.5   4.50  13.00  12.00  14.00  14.00   7.00  15.00   6.00  16.00  15.00
 10    57.0  12.00  12.00   2.00   2.00   3.00   3.00  10.00   8.00   3.00   2.00
 11    93.0   8.00   3.50   8.00   8.00   9.50  11.00  13.00  11.00   8.00  13.00
 15    80.0  14.00  11.00   4.50   5.50   5.00   8.00   5.00   5.00  13.00   9.00
 16   169.0  17.00  17.00  16.00  17.00  17.00  17.00  17.00  17.00  17.00  17.00
 17   130.5  16.00  16.00  10.00  12.50  15.00  15.00  16.00  14.00  15.00   1.00
 20   122.0  13.00  10.00  17.00  15.00  12.00  13.00  11.00  13.00  11.00   7.00
 21   101.0  15.00  15.00  14.00   9.00   6.00  12.00   8.00   9.00   5.00   8.00
 24   107.0   9.00   6.00   3.00  16.00  16.00  16.00  12.00  16.00  10.00   3.00
 25    74.0  10.00   6.00  10.00  11.00  13.00   1.00   6.00   4.00   2.00  11.00
 26    89.0   4.50   3.50  10.00   7.00   7.00   9.00   9.00  15.00  12.00  12.00
 27    83.0   1.00   6.00  13.00  12.50   9.50  10.00   4.00  10.00   7.00  10.00
-------------------------------------------------
 *** Laboratory   6 Rejected; Rank Sum   34.5 ***
 *** Laboratory  16 Rejected; Rank Sum  169.0 ***
-------------------------------------------------
```

```
File Name:  cr-8
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Freshwater
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------
 ***    Outlier Testing Results      ***
 *** Two-Sided 5% Significance Level ***
-----------------------------------------

--------------------
   - Outlier(s) -
--------------------
 Lev  Iter  Lab  Rep     Result       Mean    Std Dev    t     Crit t   n
----------------------------------------------------------------------------
  1     1    17   1      6.0000      .9067     1.7928   2.841   2.549   15
  2     1    17   1      5.0000      .6989     1.3875   3.100   2.549   15
  3     1    20   1    266.0000    22.5840    67.3498   3.614   2.549   15
  7     1    17   1     75.0000    52.7800     7.3769   3.012   2.549   15
  *     1    17   1     30.0000    94.1933    19.1742   3.348   2.549   15
----------------------------------------------------------------------------
```

```
File Name:  cr-8
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Freshwater
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------
 *** Results of Normality Testing ***
-------------------------------------------

-------------------------
   - Normality Tests -
-------------------------
               Test  Normality      Test          Critical
   Level  n    Type  Accept/Reject  Statistic     Value(s)
---------------------------------------------------------------
      1   14     W            R        .7326      .874   ---
      2   14     W     A               .9069      .874   ---
      3   14     W            R        .8205      .874   ---
      4   15     W     A               .9558      .881   ---
      5   15     W     A               .8975      .881   ---
      6   15     W     A               .9694      .881   ---
      7   14     W     A               .9597      .874   ---
      8   15     W     A               .9753      .881   ---
      9   15     W     A               .9527      .881   ---
     10   14     W     A               .9740      .874   ---
-------------------------------
 - 2 Normality Rejection(s) -
-------------------------------
```

```
File Name:  cr-8
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Freshwater
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------------
 ***         Data Removal Tracking         ***
 *** Simple Count of Remaining Data Points ***
 ***          After Removal Tests          ***
-----------------------------------------------

             Points   After Lab Ranking  After Outlier Testing
               As     -----------------  ---------------------
 Lev  Mtrx  Received     Points    %        Points       %

 ---  ----  --------  ---------  ------  ----------    ------
  1     8       17          15    88.2          14      82.4
  2     8       17          15    88.2          14      82.4
  3     8       17          15    88.2          14      82.4
  4     8       17          15    88.2          15      88.2
  5     8       17          15    88.2          15      88.2
  6     8       17          15    88.2          15      88.2
  7     8       17          15    88.2          14      82.4
  8     8       17          15    88.2          15      88.2
  9     8       17          15    88.2          15      88.2
 10     8       17          15    88.2          14      82.4
 ---  ----  --------  ---------  ------  ----------    ------
Totals:        170         150    88.2         145      85.3
--------------------------------------------------------------
```

```
File Name:  cr-8
Statistical Analysis File (.STT)


----------------------------------------
 *** Summary Performance Statistics ***
----------------------------------------
Analyte:  Cr          Matrix:  Freshwater
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

------------------------------------------------------------------------------------------------------------------------
            LEVEL:         1         2         3         4         5         6         7         8         9        10
------------------------------------------------------------------------------------------------------------------------
YOUDEN PAIRS:         Pair 1    Pair 1    Pair 2    Pair 2    Pair 3    Pair 3    Pair 4    Pair 4    Pair 5    Pair 5
                       (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)
------------------------------------------------------------------------------------------------------------------------
CONCENTRATION:         .4673     .4673    5.2673    8.2673   19.9673   24.9673   54.9673   62.9673   87.6673  100.1673
------------------------------------------------------------------------------------------------------------------------
RECOVERY:
 Observations             14        14        14        15        15        15        14        15        15        14
 Mean Result           .5429     .3916    5.1971    8.3993   20.4733   24.0400   51.1929   61.4867   88.2200   98.7786
 Bias                  .0756    -.0757    -.0702     .1320     .5060    -.9273   -3.7744   -1.4806     .5527   -1.3887
 Relative Bias %     16.1842  -16.1903   -1.3319    1.5971    2.5343   -3.7141   -6.8667   -2.3514     .6304   -1.3864
 Maximum Result       4.1000    2.1000    8.4800   11.7000   29.1000   31.3000   57.6000   83.8000  103.0000  110.0000
 Minimum Result      -1.0000    -.5000    3.9000    6.0500   14.8000   16.8000   42.5000   45.9000   77.7000   84.9000
------------------------------------------------------------------------------------------------------------------------
SINGLE OPERATOR PRECISION:   Pair 1              Pair 2              Pair 3              Pair 4              Pair 5
   Observations                  14                  14                  15                  14                  14
   Standard Deviation         .5453              1.5072              2.2747              5.6724              4.8211
   Correction Factor         1.0194              1.0194              1.0180              1.0194              1.0194
   Corrected Std Dev          .5558              1.5364              2.3156              5.7824              4.9146
   Relative Std Dev (%)    118.9486             22.4184             10.4041             10.2313              5.2666
------------------------------------------------------------------------------------------------------------------------
OVERALL PRECISION:
 Observations              14        14        14        15        15        15        14        15        15        14
 Standard Deviation    1.1504     .7405    1.2535    1.4599    3.9125    3.3588    4.2324    9.9609    7.5743    7.5038
 Correction Factor     1.0194    1.0194    1.0194    1.0180    1.0180    1.0180    1.0194    1.0180    1.0180    1.0194
 Corrected Std Dev     1.1727     .7549    1.2778    1.4862    3.9830    3.4192    4.3145   10.1402    7.7107    7.6493
 Relative Std Dev %  215.9957  192.7552   24.5874   17.6940   19.4543   14.2230    8.4278   16.4917    8.7403    7.7439
------------------------------------------------------------------------------------------------------------------------
```

```
File Name:  cr-8
Statistical Analysis File (.STT)


----------------------------------
  *** Results of Bias Testing ***
----------------------------------
 Analyte:  Cr          Matrix:  Freshwater
 Project:  AMQ-TC      Method:  GFAAS
    Date:  12/13/1995
   Units:  ug/L

------------------------------------------------------------------------
                                    Rel.     Obs    Crit   Statistically
Conc.             Mean              Bias       t       t     Significant
Level   Conc    Result      Bias     (%)   Value   Value   (1% Two-Tail)
------------------------------------------------------------------------
 1     .4673     .5429     .0756   16.18    .245   3.012         NO
 2     .4673     .3916    -.0757  -16.19    .382   3.012         NO
 3    5.2673    5.1971    -.0702   -1.33    .209   3.012         NO
 4    8.2673    8.3993     .1320    1.60    .350   2.977         NO
 5   19.9673   20.4733     .5060    2.53    .501   2.977         NO
 6   24.9673   24.0400    -.9273   -3.71   1.069   2.977         NO
 7   54.9673   51.1929   -3.7744   -6.87   3.337   3.012        YES
 8   62.9673   61.4867   -1.4806   -2.35    .576   2.977         NO
 9   87.6673   88.2200     .5527     .63    .283   2.977         NO
10  100.1673   98.7786   -1.3887   -1.39    .692   3.012         NO
------------------------------------------------------------------------
```

```
File Name:  cr-8
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***   Single Operator Precision    ***
----------------------------------------
Analyte:  Cr          Matrix:  Freshwater
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):      .7690
          Slope (b):      .0651
    =============================
                                           Single
           Sample Weights                Operator   Estimated
    Pair   Size       (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      14     49.22       .4673       .5558       .7995
      2      14     30.60      6.7673      1.5364      1.2098
      3      15     14.15     22.4673      2.3156      2.2325
      4      14      4.04     58.9673      5.7824      4.6100
      5      14      1.99     93.9173      4.9146      6.8865
    -----------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    =========================================================
      a:     1.0620      Intercept (a'):      .0602
      b:     1.0208          Slope (b'):      .0206
    =========================================================
                                                  Single
           Sample Weight               Operator   Estimated
    Pair   Size      (%)        Conc     Std Dev     Std Dev
    ---------------------------------------------------------
      1      14    19.69       .4673       .5558      1.0723
      2      14    19.69       .4673      1.5364      1.2205
      3      15    21.23      5.2673      2.3156      1.6853
      4      14    19.69      8.2673      5.7824      3.5686
      5      14    19.69     19.9673      4.9146      7.3193
    ---------------------------------------------------------
```

```
File Name:  cr-8
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***       Overall Precision        ***
----------------------------------------
Analyte:  Cr          Matrix:  Freshwater
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Overall Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):      .9477
          Slope (b):      .0934
    =============================
    Conc   Sample   Weights                 Overall   Estimated
    Level  Size        (%)        Conc     Std Dev     Std Dev
    -------------------------------------------------------------
      1      14       26.66       .4673      1.1727       .9914
      2      14       26.66       .4673       .7549       .9914
      3      14       16.57      5.2673      1.2778      1.4398
      4      15       13.93      8.2673      1.4862      1.7200
      5      15        6.57     19.9673      3.9830      2.8130
      6      15        5.11     24.9673      3.4192      3.2801
      7      14        1.63     54.9673      4.3145      6.0825
      8      15        1.42     62.9673     10.1402      6.8299
      9      15         .83     87.6673      7.7107      9.1372
     10      14         .62    100.1673      7.6493     10.3049
    -------------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    ===========================================================
      a:     1.3754      Intercept (a'):      .3187
      b:     1.0219          Slope (b'):      .0217
    ===========================================================
    Conc   Sample   Weight                 Overall   Estimated
    Level  Size       (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      14        9.62       .4673      1.1727      1.3893
      2      14        9.62       .4673       .7549      1.3893
      3      14        9.62      5.2673      1.2778      1.5415
      4      15       10.38      8.2673      1.4862      1.6449
      5      15       10.38     19.9673      3.9830      2.1191
      6      15       10.38     24.9673      3.4192      2.3614
      7      14        9.62     54.9673      4.3145      4.5211
      8      15       10.38     62.9673     10.1402      5.3761
      9      15       10.38     87.6673      7.7107      9.1771
     10      14        9.62    100.1673      7.6493     12.0292
    -----------------------------------------------------------
```

```
File Name:  cr-8
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ************  Recovery  **************
----------------------------------------
Analyte:  Cr          Matrix:  Freshwater
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Recovery ***

    - Linear Model - X = b*T + a
    =============================
      Intercept (a):      .0534
          Slope (b):      .9807
    =============================
    Conc   Sample   Weights                  Mean   Estimated
    Level  Size         (%)      Conc      Result      Result
    ----------------------------------------------------------
      1      14     31.93       .4673       .5429       .5116
      2      14     31.93       .4673       .3916       .5116
      3      14     15.14      5.2673      5.1971      5.2190
      4      15     11.36      8.2673      8.3993      8.1611
      5      15      4.25     19.9673     20.4733     19.6352
      6      15      3.13     24.9673     24.0400     24.5387
      7      14       .85     54.9673     51.1929     53.9596
      8      15       .72     62.9673     61.4867     61.8051
      9      15       .40     87.6673     88.2200     86.0283
     10      14       .30    100.1673     98.7786     98.2870
    ----------------------------------------------------------


File Name:  cr-8
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***     Precision vs Recovery      ***
----------------------------------------
Analyte:  Cr          Matrix:  Freshwater
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision vs Recovery ***
           (Obtained by Substitution)

     - Linear Model - s = f*X + e
    ==============================
        Intercept (e):      .7146
            Slope (f):      .0664
    ==============================


     - Curvilinear Model - s = e*(f**X)
    ====================================
        Intercept (e):     1.0609
                  (f):     1.0212
    ====================================



 *** Overall Precision vs Recovery ***
       (Obtained by Substitution)

     - Linear Model - s = f*X + e
     =============================
        Intercept (e):      .8933
            Slope (f):      .0953
     =============================


     - Curvilinear Model - s = e*(f**X)
     ===================================
        Intercept (e):     1.3737
                  (f):     1.0223
     ===================================
```

```
cr-9.dat

Cr     9   5    2.0000    0.0000   55.0000   74.0000  283.0000  372.0000  618.0000  697.0000  820.0000  932.0000
Cr     9   6   -7.0000  -10.0000   48.0000   70.0000  282.0000  337.0000  648.0000  732.0000  816.0000  944.0000
Cr     9   7    1.5500    1.7300   45.5000   60.0000  323.0000  407.0000  645.0000  720.0000  797.0000  895.0000
Cr     9   8    2.8000    0.9000   55.3000   75.5000  269.0000  286.0000  534.0000  601.0000  726.0000  818.0000
Cr     9  10   29.5000    4.0000   58.5000   90.5000  372.5000  430.5000  729.5000  764.5000  980.0000 1050.0000
Cr     9  15    1.1000    1.0000   47.0000   67.0000  261.0000  333.0000  532.0000  642.0000  728.0000  878.0000
Cr     9  16    8.0000   84.0000   60.0000  100.0000  378.0000  269.0000  471.0000  582.0000  644.0000  700.0000
Cr     9  17    6.0000    3.0000   66.0000   94.0000  376.0000  420.0000  690.0000  780.0000  910.0000 1249.0000
Cr     9  20   27.0000   23.0000   80.0000   90.0000  329.0000  390.0000  682.0000  735.0000  873.0000  972.0000
Cr     9  21    1.0000    0.5000   61.0000   76.0000  293.0000  378.0000  596.0000  698.0000  823.0000  905.0000
Cr     9  24    7.0000    0.0000   74.2000   67.1000  397.0000  487.0000  717.0000  548.0000  734.0000  801.0000
Cr     9  25    2.4000    0.0000   62.7000   81.4000  321.0000  409.0000  667.0000  768.0000  848.0000  949.0000
Cr     9  26    3.0000    0.0000   60.0000   73.0000  284.0000  335.0000  625.0000  670.0000  800.0000  950.0000
Cr     9  27   10.0000   10.0000   70.0000   80.0000  280.0000  390.0000  550.0000  600.0000  790.0000  810.0000
```

```
File Name:  cr-9
Data Validation File (.DA~)

******************************************************************************
***                   Parameter and Data Validation File                   ***
******************************************************************************
   Analyte:  Cr              Matrix:  Estuarine
   Project:  AMQ-TC       Matrix ID:   9
      Date:  12/13/1995      Method:  GFAAS
     Pairs:  5
     Units:  ug/L

---------------------------------------------------------------------------------------------------------------------------------
Level          1          2            3          4            5          6            7          8            9         10
---------------------------------------------------------------------------------------------------------------------------------
Spike          2.6809      .0000      56.1000    19.7000     219.0000    81.0000     269.0000    71.0000     127.0000   110.0000
Spike
Increment       .0000      .0000      56.1000    75.8000     294.8000   375.8000     644.8000   715.8000     842.8000   952.8000
---------------------------------------------------------------------------------------------------------------------------------

                 Final Concentration
         ------------------------------------------------------------------------------------------------------------------------
Lab ID         2.6809     2.6809      58.7809    78.4809     297.4809   378.4809     647.4809   718.4809     845.4809   955.4809
---------------------------------------------------------------------------------------------------------------------------------
    5          2.0000      .0000      55.0000    74.0000     283.0000   372.0000     618.0000   697.0000     820.0000   932.0000
    6         -7.0000   -10.0000      48.0000    70.0000     282.0000   337.0000     648.0000   732.0000     816.0000   944.0000
    7          1.5500     1.7300      45.5000    60.0000     323.0000   407.0000     645.0000   720.0000     797.0000   895.0000
    8          2.8000      .9000      55.3000    75.5000     269.0000   286.0000     534.0000   601.0000     726.0000   818.0000
   10    r    29.5000r    4.0000 r    58.5000r   90.5000 r   372.5000r  430.5000 r   729.5000r  764.5000 r   980.0000r 1050.0000
   15    !     1.1000!    1.0000 !    47.0000!   67.0000 !   261.0000!  333.0000 !   532.0000!  642.0000 !   728.0000!  878.0000
   16          8.0000o   84.0000      60.0000   100.0000     378.0000   269.0000     471.0000   582.0000     644.0000   700.0000
   17    r     6.0000r    3.0000 r    66.0000r   94.0000 r   376.0000r  420.0000 r   690.0000r  780.0000 r   910.0000r 1249.0000
   20    o    27.0000?   23.0000 !    80.0000!   90.0000 !   329.0000!  390.0000 !   682.0000!  735.0000 !   873.0000!  972.0000
   21          1.0000      .5000      61.0000    76.0000     293.0000   378.0000     596.0000   698.0000     823.0000   905.0000
   24          7.0000      .0000      74.2000    67.1000     397.0000   487.0000     717.0000   548.0000     734.0000   801.0000
   25          2.4000      .0000      62.7000    81.4000     321.0000   409.0000     667.0000   768.0000     848.0000   949.0000
   26          3.0000      .0000      60.0000    73.0000     284.0000   335.0000     625.0000   670.0000     800.0000   950.0000
   27         10.0000    10.0000      70.0000    80.0000     280.0000   390.0000     550.0000   600.0000     790.0000   810.0000
---------------------------------------------------------------------------------------------------------------------------------
```

```
cr-9.daf

Cr     9   5    2.0000     .0000   55.0000   74.0000  283.0000  372.0000  618.0000  697.0000  820.0000  932.0000
Cr     9   6   -7.0000  -10.0000   48.0000   70.0000  282.0000  337.0000  648.0000  732.0000  816.0000  944.0000
Cr     9   7    1.5500    1.7300   45.5000   60.0000  323.0000  407.0000  645.0000  720.0000  797.0000  895.0000
Cr     9   8    2.8000     .9000   55.3000   75.5000  269.0000  286.0000  534.0000  601.0000  726.0000  818.0000
Cr     9  15    1.1000    1.0000   47.0000   67.0000  261.0000  333.0000  532.0000  642.0000  728.0000  878.0000
Cr     9  16    8.0000o            60.0000  100.0000  378.0000  269.0000  471.0000  582.0000  644.0000  700.0000
Cr     9  20 o           23.0000   80.0000   90.0000  329.0000  390.0000  682.0000  735.0000  873.0000  972.0000
Cr     9  21    1.0000     .5000   61.0000   76.0000  293.0000  378.0000  596.0000  698.0000  823.0000  905.0000
Cr     9  24    7.0000     .0000   74.2000   67.1000  397.0000  487.0000  717.0000  548.0000  734.0000  801.0000
Cr     9  25    2.4000     .0000   62.7000   81.4000  321.0000  409.0000  667.0000  768.0000  848.0000  949.0000
Cr     9  26    3.0000     .0000   60.0000   73.0000  284.0000  335.0000  625.0000  670.0000  800.0000  950.0000
Cr     9  27   10.0000   10.0000   70.0000   80.0000  280.0000  390.0000  550.0000  600.0000  790.0000  810.0000
```

```
File Name:  cr-9
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Estuarine
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------------------------
 ***        Results of 5x - 1/5x Mean Error Check        ***
 ***         Questionable Data (Positive Values)         ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean
 Lev   No   No     Result     Result                   Ratio
-------------------------------------------------------------
  1     15  1      7.2393     1.1000                   .15
  1     21  1      7.2393     1.0000                   .14
  2      7  1      9.1521     1.7300                   .19
  2      8  1      9.1521      .9000                   .10
  2     15  1      9.1521     1.0000                   .11
  2     16  1      9.1521    84.0000                  9.18
  2     21  1      9.1521      .5000                   .05
-------------------------------------------------------------
Total Number of Questionable Observations:     7


-------------------------------------------------------------
 ***        Results of Factor of 5 Error Check           ***
 ***          Questionable Data (All Values)             ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean                   Mean    Obs
 Lev   No   No     Result     Result      Dev     Dev   Ratio
-------------------------------------------------------------
  2    16   1      8.4379    84.0000   13.098   75.562  5.77
-------------------------------------------------------------
Total Number of Questionable Observations:     1


File Name:  cr-9
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Estuarine
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
----------------------------------------------
 ***      Laboratory Ranking Results      ***
 ***   Two-Tailed 5% Significance Level   ***
 ***-------------------------------------***
 ***     Upper Critical Value:    112.0   ***
 ***     Lower Critical Value:     38.0   ***
----------------------------------------------

      Ranks
     -----------------------------------------------------------------------------
       Rank  Level  Level  Level  Level  Level  Level  Level  Level  Level  Level
Lab    Sums    1      2      3      4      5      6      7      8      9     10
---- -----------------------------------------------------------------------------
  5    59.5   5.00   3.50   4.00   6.00   5.00   6.00   6.00   7.00   9.00   8.00
  6    54.0   1.00   1.00   3.00   4.00   4.00   5.00   9.00  10.00   8.00   9.00
  7    63.0   4.00   9.00   1.00   1.00   9.00  10.00   8.00   9.00   6.00   6.00
  8    43.0   7.00   7.00   5.00   7.00   2.00   2.00   3.00   4.00   2.00   4.00
 10   120.0  14.00  11.00   6.00  12.00  11.00  13.00  14.00  12.00  14.00  13.00
 15    34.0   3.00   8.00   2.00   2.00   1.00   3.00   2.00   5.00   3.00   5.00
 16    65.5  11.00  14.00   7.50  14.00  13.00   1.00   1.00   2.00   1.00   1.00
 17   120.0   9.00  10.00  11.00  13.00  12.00  12.00  12.00  14.00  13.00  14.00
 20   115.5  13.00  13.00  14.00  11.00  10.00   8.50  11.00  11.00  12.00  12.00
 21    69.0   2.00   6.00   9.00   8.00   7.00   7.00   5.00   8.00  10.00   7.00
 24    77.5  10.00   3.50  13.00   3.00  14.00  14.00  13.00   1.00   4.00   2.00
 25    92.5   6.00   3.50  10.00  10.00   8.00  11.00  10.00  13.00  11.00  10.00
 26    65.0   8.00   3.50   7.50   5.00   6.00   4.00   7.00   6.00   7.00  11.00
 27    71.5  12.00  12.00  12.00   9.00   3.00   8.50   4.00   3.00   5.00   3.00
-------------------------------------------------
 *** Laboratory  10 Rejected; Rank Sum  120.0 ***
 *** Laboratory  17 Rejected; Rank Sum  120.0 ***
-------------------------------------------------

File Name:  cr-9
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Estuarine
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------
 ***    Outlier Testing Results      ***
 *** Two-Sided 5% Significance Level ***
-----------------------------------------

--------------------
   - Outlier(s) -
--------------------
 Lev  Iter  Lab  Rep     Result       Mean    Std Dev    t     Crit t   n
----------------------------------------------------------------------------
  1     1    20   1     27.0000     4.9042     8.1665   2.706   2.412   12
  2     1    16   1     84.0000     9.2608    24.7917   3.015   2.412   12
----------------------------------------------------------------------------
```

```
File Name:  cr-9
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Estuarine
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------
 *** Results of Normality Testing ***
-------------------------------------------

-------------------------
   - Normality Tests -
-------------------------
               Test  Normality      Test          Critical
   Level  n    Type  Accept/Reject  Statistic     Value(s)
---------------------------------------------------------------
     1    11     W     A              .8985      .850   ---
     2    11     W            R       .7518      .850   ---
     3    12     W     A              .9484      .859   ---
     4    12     W     A              .9451      .859   ---
     5    12     W     A              .8659      .859   ---
     6    12     W     A              .9590      .859   ---
     7    12     W     A              .9654      .859   ---
     8    12     W     A              .9455      .859   ---
     9    12     W     A              .9299      .859   ---
    10    12     W     A              .8982      .859   ---
-------------------------------
 - 1 Normality Rejection(s) -
-------------------------------


File Name:  cr-9
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Estuarine
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------------
 ***         Data Removal Tracking         ***
 *** Simple Count of Remaining Data Points ***
 ***          After Removal Tests          ***
-----------------------------------------------

             Points   After Lab Ranking  After Outlier Testing
               As     -----------------  ---------------------
 Lev  Mtrx  Received     Points    %         Points       %

 ---  ----  --------  ---------  ------  ----------     ------
  1     9       14          12    85.7          11       78.6
  2     9       14          12    85.7          11       78.6
  3     9       14          12    85.7          12       85.7
  4     9       14          12    85.7          12       85.7
  5     9       14          12    85.7          12       85.7
  6     9       14          12    85.7          12       85.7
  7     9       14          12    85.7          12       85.7
  8     9       14          12    85.7          12       85.7
  9     9       14          12    85.7          12       85.7
 10     9       14          12    85.7          12       85.7
 ---  ----  --------  ---------  ------  ----------     ------
Totals:        140         120    85.7         118       84.3
--------------------------------------------------------------
```

```
File Name:  cr-9
Statistical Analysis File (.STT)


----------------------------------------
 *** Summary Performance Statistics ***
----------------------------------------
Analyte:  Cr          Matrix:  Estuarine
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

------------------------------------------------------------------------------------------------------------------------
            LEVEL:         1         2         3         4         5         6         7         8         9        10
------------------------------------------------------------------------------------------------------------------------
YOUDEN PAIRS:         Pair 1    Pair 1    Pair 2    Pair 2    Pair 3    Pair 3    Pair 4    Pair 4    Pair 5    Pair 5
                       (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)
------------------------------------------------------------------------------------------------------------------------
CONCENTRATION:        2.6809    2.6809   58.7809   78.4809  297.4809  378.4809  647.4809  718.4809  845.4809  955.4809
------------------------------------------------------------------------------------------------------------------------
RECOVERY:
 Observations             11        11        12        12        12        12        12        12        12        12
 Mean Result          2.8955    2.4664   59.8917   76.1667  308.3333  366.0833  607.0833  666.0833  783.2500  879.5000
 Bias                  .2146    -.2145    1.1108   -2.3142   10.8524  -12.3976  -40.3976  -52.3976  -62.2309  -75.9809
 Relative Bias %      8.0031   -8.0024    1.8897   -2.9488    3.6481   -3.2756   -6.2392   -7.2928   -7.3604   -7.9521
 Maximum Result      10.0000   23.0000   80.0000  100.0000  397.0000  487.0000  717.0000  768.0000  873.0000  972.0000
 Minimum Result      -7.0000  -10.0000   45.5000   60.0000  261.0000  269.0000  471.0000  548.0000  644.0000  700.0000
------------------------------------------------------------------------------------------------------------------------
SINGLE OPERATOR PRECISION:   Pair 1              Pair 2              Pair 3              Pair 4              Pair 5
   Observations                  10                  12                  12                  12                  12
   Standard Deviation        1.5234              7.6244             40.9136             53.3258             26.6102
   Correction Factor         1.0281              1.0230              1.0230              1.0230              1.0230
   Corrected Std Dev         1.5662              7.7994             41.8528             54.5499             27.2210
   Relative Std Dev (%)     58.4221             11.4648             12.4115              8.5692              3.2742
------------------------------------------------------------------------------------------------------------------------
OVERALL PRECISION:
 Observations              11        11        12        12        12        12        12        12        12        12
 Standard Deviation    4.4832    8.1679   10.7877   10.7969   42.9277   58.9321   72.4349   70.4369   63.8978   81.5537
 Correction Factor     1.0253    1.0253    1.0230    1.0230    1.0230    1.0230    1.0230    1.0230    1.0230    1.0230
 Corrected Std Dev     4.5965    8.3743   11.0354   11.0447   43.9131   60.2849   74.0977   72.0538   65.3646   83.4258
 Relative Std Dev %  158.7495  339.5400   18.4256   14.5007   14.2421   16.4675   12.2055   10.8175    8.3453    9.4856
------------------------------------------------------------------------------------------------------------------------
```

```
File Name:  cr-9
Statistical Analysis File (.STT)


----------------------------------
  *** Results of Bias Testing ***
----------------------------------
 Analyte:  Cr          Matrix:  Estuarine
 Project:  AMQ-TC      Method:  GFAAS
    Date:  12/13/1995
   Units:  ug/L

------------------------------------------------------------------------
                                    Rel.     Obs    Crit   Statistically
Conc.             Mean              Bias       t       t     Significant
Level   Conc    Result      Bias     (%)   Value   Value   (1% Two-Tail)
------------------------------------------------------------------------
 1    2.6809    2.8955     .2146    8.00    .159   3.169         NO
 2    2.6809    2.4664    -.2145   -8.00    .087   3.169         NO
 3   58.7809   59.8917    1.1108    1.89    .357   3.106         NO
 4   78.4809   76.1667   -2.3142   -2.95    .743   3.106         NO
 5  297.4809  308.3333   10.8524    3.65    .876   3.106         NO
 6  378.4809  366.0833  -12.3976   -3.28    .729   3.106         NO
 7  647.4809  607.0833  -40.3976   -6.24   1.932   3.106         NO
 8  718.4809  666.0833  -52.3976   -7.29   2.577   3.106         NO
 9  845.4809  783.2500  -62.2309   -7.36   3.374   3.106        YES
10  955.4809  879.5000  -75.9809   -7.95   3.227   3.106        YES
------------------------------------------------------------------------
```

```
File Name:  cr-9
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***   Single Operator Precision    ***
----------------------------------------
Analyte:  Cr          Matrix:  Estuarine
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):     4.3037
          Slope (b):      .0605
    =============================
                                           Single
           Sample Weights                Operator   Estimated
    Pair   Size       (%)         Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      10     42.58      2.6809      1.5662      4.4659
      2      12     35.95     68.6309      7.7994      8.4565
      3      12     12.49    337.9809     41.8528     24.7549
      4      12      5.36    682.9809     54.5499     45.6308
      5      12      3.62    900.4809     27.2210     58.7917
    -----------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    =========================================================
      a:     5.3611      Intercept (a'):     1.6792
      b:     1.0027          Slope (b'):      .0027
    =========================================================
                                                  Single
           Sample Weight               Operator   Estimated
    Pair   Size      (%)        Conc     Std Dev     Std Dev
    ---------------------------------------------------------
      1      10    16.92      2.6809      1.5662      5.4000
      2      12    20.77      2.6809      7.7994      6.4510
      3      12    20.77     58.7809     41.8528     13.3373
      4      12    20.77     78.4809     54.5499     33.8145
      5      12    20.77    297.4809     27.2210     60.7886
    ---------------------------------------------------------

File Name:  cr-9
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***       Overall Precision        ***
----------------------------------------
Analyte:  Cr          Matrix:  Estuarine
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Overall Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):     6.1557
          Slope (b):      .0976
    =============================
    Conc   Sample   Weights                 Overall   Estimated
    Level  Size         (%)        Conc     Std Dev     Std Dev
    -------------------------------------------------------------
      1      11       30.07      2.6809      4.5965      6.4173
      2      11       30.07      2.6809      8.3743      6.4173
      3      12       16.89     58.7809     11.0354     11.8909
      4      12       13.95     78.4809     11.0447     13.8130
      5      12        3.44    297.4809     43.9131     35.1805
      6      12        2.44    378.4809     60.2849     43.0835
      7      12        1.05    647.4809     74.0977     69.3294
      8      12         .89    718.4809     72.0538     76.2567
      9      12         .67    845.4809     65.3646     88.6479
     10      12         .54    955.4809     83.4258     99.3805
    -------------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    ===========================================================
      a:     9.9583      Intercept (a'):     2.2984
      b:     1.0027          Slope (b'):      .0027
    ===========================================================
    Conc   Sample   Weight                 Overall   Estimated
    Level  Size        (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      11       9.24      2.6809      4.5965     10.0297
      2      11       9.24      2.6809      8.3743     10.0297
      3      12      10.19     58.7809     11.0354     11.6480
      4      12      10.19     78.4809     11.0447     12.2762
      5      12      10.19    297.4809     43.9131     22.0118
      6      12      10.19    378.4809     60.2849     27.3181
      7      12      10.19    647.4809     74.0977     55.9683
      8      12      10.19    718.4809     72.0538     67.6328
      9      12      10.19    845.4809     65.3646     94.8896
     10      12      10.19    955.4809     83.4258    127.2314
    -----------------------------------------------------------
```

```
File Name:  cr-9
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ************  Recovery  **************
----------------------------------------
Analyte:  Cr          Matrix:  Estuarine
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Recovery ***

    - Linear Model - X = b*T + a
    =============================
      Intercept (a):      .9728
          Slope (b):      .9501
    =============================
    Conc   Sample   Weights                  Mean   Estimated
    Level  Size         (%)      Conc      Result      Result
    ----------------------------------------------------------
      1      11     37.86      2.6809      2.8955      3.5200
      2      11     37.86      2.6809      2.4664      3.5200
      3      12     12.03     58.7809     59.8917     56.8231
      4      12      8.92     78.4809     76.1667     75.5409
      5      12      1.37    297.4809    308.3333    283.6223
      6      12       .92    378.4809    366.0833    360.5840
      7      12       .35    647.4809    607.0833    616.1726
      8      12       .29    718.4809    666.0833    683.6328
      9      12       .22    845.4809    783.2500    804.3010
     10      12       .17    955.4809    879.5000    908.8168
    ----------------------------------------------------------


File Name:  cr-9
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***     Precision vs Recovery      ***
----------------------------------------
Analyte:  Cr          Matrix:  Estuarine
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision vs Recovery ***
           (Obtained by Substitution)

     - Linear Model - s = f*X + e
    ==============================
        Intercept (e):     3.2799
            Slope (f):      .0637
    ==============================


     - Curvilinear Model - s = e*(f**X)
    ===================================
        Intercept (e):     5.3463
                  (f):     1.0028
    ===================================



 *** Overall Precision vs Recovery ***
       (Obtained by Substitution)

     - Linear Model - s = f*X + e
     =============================
        Intercept (e):     5.1319
            Slope (f):      .1027
     =============================


     - Curvilinear Model - s = e*(f**X)
     ==================================
        Intercept (e):     9.9311
                  (f):     1.0028
     ==================================
```

```
cr-10.dat

Cr    10   1    12.4000   11.4000   40.5000   58.1000  165.1000  214.7000  399.0000  440.0000 1123.0000 1022.0000
Cr    10   2     2.0000    3.0000   47.0000   66.0000  210.0000  279.0000  430.0000  410.0000  744.0000  732.0000
Cr    10   5     3.0000    3.0000   41.0000   59.0000  180.0000  247.0000  378.0000  436.0000  752.0000  817.0000
Cr    10   6     0.0000   -7.0000   39.0000   54.0000  206.0000  290.0000  446.0000  505.0000  863.0000  951.0000
Cr    10   7     5.1200    4.8200   43.4000   62.0000  206.0000  275.0000  418.0000  468.0000  796.0000  822.0000
Cr    10   8     0.9000    0.4000   30.3000   52.2000  172.0000  257.0000  394.0000  479.0000  794.0000  930.0000
Cr    10  10    42.5000  100.0000  100.5000   73.5000  308.0000  343.0000  463.0000  466.0000  971.0000 1072.5000
Cr    10  11     7.1000    8.2000   51.7000   69.8000  215.0000  276.0000  451.0000  505.0000  902.0000  990.0000
Cr    10  15     3.9000    4.1000   40.0000   59.0000  192.0000  247.0000  396.0000  413.0000  718.0000  855.0000
Cr    10  16    22.2000    8.9000   54.4000  111.0000  233.0000  322.0000  478.0000  460.0000  830.0000  910.0000
Cr    10  17     6.0000    4.0000   53.0000   69.0000  223.0000  303.0000  512.0000  580.0000 1020.0000 1211.0000
Cr    10  20    24.0000   18.0000   87.0000   96.0000  266.0000  343.0000  507.0000  563.0000  937.0000 1052.0000
Cr    10  21     2.9000    2.0000   36.0000   53.0000  171.0000  244.0000  376.0000  439.0000  765.0000  869.0000
Cr    10  24     5.2000    0.0000   32.9000   73.4000  230.0000  258.0000  487.0000  496.0000  450.0000  106.0000
Cr    10  25     0.0000    2.4000   58.3000   81.4000  269.0000  295.0000  459.0000  529.0000 1020.0000  949.0000
Cr    10  26     4.0000    4.0000   53.0000   81.0000  206.0000  268.0000  460.0000  490.0000  890.0000  950.0000
Cr    10  27    10.0000   20.0000   40.0000   80.0000  170.0000  220.0000  300.0000  460.0000  780.0000  870.0000
```

```
File Name:  cr-10
Data Validation File (.DA~)

******************************************************************************
***                   Parameter and Data Validation File                   ***
******************************************************************************
   Analyte:  Cr              Matrix:  Acid Mine Drainage
   Project:  AMQ-TC       Matrix ID:  10
      Date:  12/13/1995      Method:  GFAAS
     Pairs:  5
     Units:  ug/L

---------------------------------------------------------------------------------------------------------------------------------
Level          1          2            3          4            5          6            7          8            9         10
---------------------------------------------------------------------------------------------------------------------------------
Spike         4.6978      .0000      45.9000    19.6000     150.0000    70.0000     167.0000    64.0000     391.0000    89.0000
Spike
Increment      .0000      .0000      45.9000    65.5000     215.5000   285.5000     452.5000   516.5000     907.5000   996.5000
---------------------------------------------------------------------------------------------------------------------------------

                 Final Concentration
         ------------------------------------------------------------------------------------------------------------------------
Lab ID        4.6978     4.6978      50.5978    70.1978     220.1978   290.1978     457.1978   521.1978     912.1978  1001.1980
---------------------------------------------------------------------------------------------------------------------------------
    1        12.4000    11.4000      40.5000    58.1000     165.1000   214.7000     399.0000   440.0000    1123.0000  1022.0000
    2         2.0000     3.0000      47.0000    66.0000     210.0000   279.0000     430.0000   410.0000     744.0000   732.0000
    5         3.0000     3.0000      41.0000    59.0000     180.0000   247.0000     378.0000   436.0000     752.0000   817.0000
    6          .0000    -7.0000      39.0000    54.0000     206.0000   290.0000     446.0000   505.0000     863.0000   951.0000
    7         5.1200     4.8200      43.4000    62.0000     206.0000   275.0000     418.0000   468.0000     796.0000   822.0000
    8          .9000      .4000      30.3000    52.2000     172.0000   257.0000     394.0000   479.0000     794.0000   930.0000
   10    r   42.5000r  100.0000  r  100.5000r   73.5000  r  308.0000r  343.0000  r  463.0000r  466.0000  r  971.0000r 1072.5000
   11         7.1000     8.2000      51.7000    69.8000     215.0000   276.0000     451.0000   505.0000     902.0000   990.0000
   15         3.9000     4.1000      40.0000    59.0000     192.0000   247.0000     396.0000   413.0000     718.0000   855.0000
   16    o   22.2000     8.9000      54.4000o  111.0000     233.0000   322.0000     478.0000   460.0000     830.0000   910.0000
   17         6.0000     4.0000      53.0000    69.0000     223.0000   303.0000     512.0000   580.0000    1020.0000  1211.0000
   20    r   24.0000r   18.0000  r   87.0000r   96.0000  r  266.0000r  343.0000  r  507.0000r  563.0000  r  937.0000r 1052.0000
   21    r    2.9000r    2.0000  r   36.0000r   53.0000  r  171.0000r  244.0000  r  376.0000r  439.0000  r  765.0000r  869.0000
   24         5.2000      .0000      32.9000    73.4000     230.0000   258.0000     487.0000   496.0000     450.0000o  106.0000
   25          .0000     2.4000      58.3000    81.4000     269.0000   295.0000     459.0000   529.0000    1020.0000   949.0000
   26         4.0000     4.0000      53.0000    81.0000     206.0000   268.0000     460.0000   490.0000     890.0000   950.0000
   27        10.0000    20.0000      40.0000    80.0000     170.0000   220.0000     300.0000   460.0000     780.0000   870.0000
---------------------------------------------------------------------------------------------------------------------------------
```

```
cr-10.daf

Cr    10   1    12.4000   11.4000   40.5000   58.1000  165.1000  214.7000  399.0000  440.0000 1123.0000 1022.0000
Cr    10   2     2.0000    3.0000   47.0000   66.0000  210.0000  279.0000  430.0000  410.0000  744.0000  732.0000
Cr    10   5     3.0000    3.0000   41.0000   59.0000  180.0000  247.0000  378.0000  436.0000  752.0000  817.0000
Cr    10   6      .0000   -7.0000   39.0000   54.0000  206.0000  290.0000  446.0000  505.0000  863.0000  951.0000
Cr    10   7     5.1200    4.8200   43.4000   62.0000  206.0000  275.0000  418.0000  468.0000  796.0000  822.0000
Cr    10   8      .9000     .4000   30.3000   52.2000  172.0000  257.0000  394.0000  479.0000  794.0000  930.0000
Cr    10  11     7.1000    8.2000   51.7000   69.8000  215.0000  276.0000  451.0000  505.0000  902.0000  990.0000
Cr    10  15     3.9000    4.1000   40.0000   59.0000  192.0000  247.0000  396.0000  413.0000  718.0000  855.0000
Cr    10  16 o             8.9000   54.4000o           233.0000  322.0000  478.0000  460.0000  830.0000  910.0000
Cr    10  17     6.0000    4.0000   53.0000   69.0000  223.0000  303.0000  512.0000  580.0000 1020.0000 1211.0000
Cr    10  24     5.2000     .0000   32.9000   73.4000  230.0000  258.0000  487.0000  496.0000  450.0000o
Cr    10  25      .0000    2.4000   58.3000   81.4000  269.0000  295.0000  459.0000  529.0000 1020.0000  949.0000
Cr    10  26     4.0000    4.0000   53.0000   81.0000  206.0000  268.0000  460.0000  490.0000  890.0000  950.0000
Cr    10  27    10.0000   20.0000   40.0000   80.0000  170.0000  220.0000  300.0000  460.0000  780.0000  870.0000
```

```
File Name:  cr-10
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Acid Mine Drainage
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------------------------
 ***        Results of 5x - 1/5x Mean Error Check        ***
 ***         Questionable Data (Positive Values)         ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean
 Lev   No   No     Result     Result                   Ratio
-------------------------------------------------------------
   1      8  1      8.8953      .9000                   .10
   2      8  1     11.4247      .4000                   .04
   2     10  1     11.4247   100.0000                  8.75
   2     21  1     11.4247     2.0000                   .18
  10     24  1    888.7353   106.0000                   .12
-------------------------------------------------------------
Total Number of Questionable Observations:     5


-------------------------------------------------------------
 ***        Results of Factor of 5 Error Check           ***
 ***          Questionable Data (All Values)             ***
-------------------------------------------------------------
 Conc  Lab  Rep     Mean                Mean    Obs
 Lev   No   No     Result     Result     Dev     Dev   Ratio
-------------------------------------------------------------
   2    10   1     11.0129   100.0000   12.394   88.987  7.18
  10    24   1    888.7353   106.0000  135.311  782.735  5.78
-------------------------------------------------------------
Total Number of Questionable Observations:     2


File Name:  cr-10
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Acid Mine Drainage
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
----------------------------------------------
 ***      Laboratory Ranking Results      ***
 ***   Two-Tailed 5% Significance Level   ***
 ***--------------------------------------***
 ***     Upper Critical Value:    135.0   ***
 ***     Lower Critical Value:     45.0   ***
----------------------------------------------

      Ranks
     ------------------------------------------------------------------------
       Rank  Level  Level  Level  Level  Level  Level  Level  Level  Level  Level
Lab    Sums    1      2      3      4      5      6      7      8      9     10
---- ------------------------------------------------------------------------
  1    83.0  14.00  14.00   7.00   4.00   1.00   1.00   6.00   5.00  17.00  14.00
  2    63.5   4.00   6.50  10.00   8.00  10.00  11.00   8.00   1.00   3.00   2.00
  5    48.5   6.00   6.50   8.00   5.50   5.00   4.50   3.00   3.00   4.00   3.00
  6    74.0   1.50   1.00   4.00   3.00   8.00  12.00   9.00  13.50  10.00  12.00
  7    81.0   9.00  11.00   9.00   7.00   8.00   9.00   7.00   9.00   8.00   4.00
  8    48.0   3.00   3.00   1.00   1.00   4.00   6.00   4.00  10.00   7.00   9.00
 10   147.5  17.00  17.00  17.00  12.00  17.00  16.50  13.00   8.00  14.00  16.00
 11   114.5  12.00  12.00  11.00  10.00  11.00  10.00  10.00  13.50  12.00  13.00
 15    52.5   7.00  10.00   5.50   5.50   6.00   4.50   5.00   2.00   2.00   5.00
 16   125.5  15.00  13.00  14.00  17.00  14.00  15.00  14.00   6.50   9.00   8.00
 17   133.5  11.00   8.50  12.50   9.00  12.00  14.00  17.00  17.00  15.50  17.00
 20   154.5  16.00  15.00  16.00  16.00  15.00  16.50  16.00  16.00  13.00  15.00
 21    37.0   5.00   4.00   3.00   2.00   3.00   3.00   2.00   4.00   5.00   6.00
 24    74.0  10.00   2.00   2.00  11.00  13.00   7.00  15.00  12.00   1.00   1.00
 25   117.0   1.50   5.00  15.00  15.00  16.00  13.00  11.00  15.00  15.50  10.00
 26   104.0   8.00   8.50  12.50  14.00   8.00   8.00  12.00  11.00  11.00  11.00
 27    72.0  13.00  16.00   5.50  13.00   2.00   2.00   1.00   6.50   6.00   7.00
-------------------------------------------------
 *** Laboratory  10 Rejected; Rank Sum  147.5 ***
 *** Laboratory  20 Rejected; Rank Sum  154.5 ***
 *** Laboratory  21 Rejected; Rank Sum   37.0 ***
-------------------------------------------------

File Name:  cr-10
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Acid Mine Drainage
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------
 ***    Outlier Testing Results      ***
 *** Two-Sided 5% Significance Level ***
-----------------------------------------

--------------------
   - Outlier(s) -
--------------------
 Lev  Iter  Lab  Rep     Result       Mean    Std Dev    t     Crit t   n
-----------------------------------------------------------------------------
   1     1    16   1     22.2000     5.8443     5.9037   2.770   2.507   14
   4     1    16   1    111.0000    69.7071    15.3918   2.683   2.507   14
   *     1    24   1    106.0000   865.3571   245.8835   3.088   2.507   14
-----------------------------------------------------------------------------
```

```
File Name:  cr-10
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Acid Mine Drainage
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-------------------------------------------
 *** Results of Normality Testing ***
-------------------------------------------

-------------------------
   - Normality Tests -
-------------------------
               Test  Normality      Test          Critical
   Level  n    Type  Accept/Reject  Statistic     Value(s)
---------------------------------------------------------------
     1    13     W     A               .9402      .866   ---
     2    14     W     A               .9186      .874   ---
     3    14     W     A               .9451      .874   ---
     4    13     W     A               .9258      .866   ---
     5    14     W     A               .9504      .874   ---
     6    14     W     A               .9790      .874   ---
     7    14     W     A               .9524      .874   ---
     8    14     W     A               .9631      .874   ---
     9    14     W     A               .9405      .874   ---
    10    13     W     A               .9345      .866   ---
-------------------------------
 - 0 Normality Rejection(s) -
-------------------------------
```

```
File Name:  cr-10
Data Preparation File (.PRP)


Analyte:  Cr     Matrix:  Acid Mine Drainage
Project:  AMQ-TC
   Date:  12/13/1995
  Units:  ug/L
-----------------------------------------------
 ***        Data Removal Tracking         ***
 *** Simple Count of Remaining Data Points ***
 ***         After Removal Tests           ***
-----------------------------------------------

             Points   After Lab Ranking  After Outlier Testing
               As     -----------------  ---------------------
 Lev  Mtrx  Received     Points    %         Points       %

 ---  ----  --------  ---------  ------  ----------     ------
  1    10       17          14    82.4          13       76.5
  2    10       17          14    82.4          14       82.4
  3    10       17          14    82.4          14       82.4
  4    10       17          14    82.4          13       76.5
  5    10       17          14    82.4          14       82.4
  6    10       17          14    82.4          14       82.4
  7    10       17          14    82.4          14       82.4
  8    10       17          14    82.4          14       82.4
  9    10       17          14    82.4          14       82.4
 10    10       17          14    82.4          13       76.5
 ---  ----  --------  ---------  ------  ----------     ------
Totals:        170         140    82.4         137       80.6
--------------------------------------------------------------
```

```
File Name:  cr-10
Statistical Analysis File (.STT)


----------------------------------------
 *** Summary Performance Statistics ***
----------------------------------------
Analyte:  Cr          Matrix:  Acid Mine Drainage
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

------------------------------------------------------------------------------------------------------------------------
            LEVEL:         1         2         3         4         5         6         7         8         9        10
------------------------------------------------------------------------------------------------------------------------
YOUDEN PAIRS:         Pair 1    Pair 1    Pair 2    Pair 2    Pair 3    Pair 3    Pair 4    Pair 4    Pair 5    Pair 5
                       (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)     (Low)    (High)
------------------------------------------------------------------------------------------------------------------------
CONCENTRATION:        4.6978    4.6978   50.5978   70.1978  220.1978  290.1978  457.1978  521.1978  912.1978 1001.1980
------------------------------------------------------------------------------------------------------------------------
RECOVERY:
 Observations             13        14        14        13        14        14        14        14        14        13
 Mean Result          4.5862    4.8014   44.6071   66.5308  205.5072  267.9786  429.1429  476.5000  834.4286  923.7692
 Bias                 -.1116     .1036   -5.9907   -3.6670  -14.6906  -22.2192  -28.0550  -44.6978  -77.7692  -77.4286
 Relative Bias %     -2.3766    2.2059  -11.8398   -5.2238   -6.6716   -7.6566   -6.1363   -8.5760   -8.5255   -7.7336
 Maximum Result      12.4000   20.0000   58.3000   81.4000  269.0000  322.0000  512.0000  580.0000 1123.0000 1211.0000
 Minimum Result        .0000   -7.0000   30.3000   52.2000  165.1000  214.7000  300.0000  410.0000  450.0000  732.0000
------------------------------------------------------------------------------------------------------------------------
SINGLE OPERATOR PRECISION:   Pair 1              Pair 2              Pair 3              Pair 4              Pair 5
   Observations                  13                  13                  14                  14                  13
   Standard Deviation        2.8082              5.9953             13.8476             32.1578             58.1594
   Correction Factor         1.0210              1.0210              1.0194              1.0194              1.0210
   Corrected Std Dev         2.8672              6.1214             14.1162             32.7816             59.3823
   Relative Std Dev (%)     61.0336             11.0969              5.9627              7.2394              6.7676
------------------------------------------------------------------------------------------------------------------------
OVERALL PRECISION:
 Observations              13        14        14        13        14        14        14        14        14        13
 Standard Deviation    3.7083    6.1932    8.4457   10.1798   28.6267   30.1738   53.9699   46.1648  162.4390  117.2548
 Correction Factor     1.0210    1.0194    1.0194    1.0210    1.0194    1.0194    1.0194    1.0194    1.0194    1.0210
 Corrected Std Dev     3.7863    6.3133    8.6095   10.3938   29.1820   30.7591   55.0168   47.0603  165.5899  119.7204
 Relative Std Dev %   82.5589  131.4881   19.3008   15.6226   14.2000   11.4782   12.8202    9.8762   19.8447   12.9600
------------------------------------------------------------------------------------------------------------------------
```

```
File Name:  cr-10
Statistical Analysis File (.STT)


----------------------------------
  *** Results of Bias Testing ***
----------------------------------
 Analyte:  Cr          Matrix:  Acid Mine Drainage
 Project:  AMQ-TC      Method:  GFAAS
    Date:  12/13/1995
   Units:  ug/L

------------------------------------------------------------------------
                                    Rel.    Obs     Crit   Statistically
Conc.             Mean              Bias      t        t     Significant
Level   Conc    Result      Bias     (%)   Value   Value   (1% Two-Tail)
------------------------------------------------------------------------
 1    4.6978    4.5862    -.1116   -2.38    .109   3.055         NO
 2    4.6978    4.8014     .1036    2.21    .063   3.012         NO
 3   50.5978   44.6071   -5.9907  -11.84   2.654   3.012         NO
 4   70.1978   66.5308   -3.6670   -5.22   1.299   3.055         NO
 5  220.1978  205.5072  -14.6906   -6.67   1.920   3.012         NO
 6  290.1978  267.9786  -22.2192   -7.66   2.755   3.012         NO
 7  457.1978  429.1429  -28.0550   -6.14   1.945   3.012         NO
 8  521.1978  476.5000  -44.6978   -8.58   3.623   3.012        YES
 9  912.1978  834.4286  -77.7692   -8.53   1.791   3.012         NO
10 1001.1980  923.7692  -77.4286   -7.73   2.381   3.055         NO
------------------------------------------------------------------------
```

```
File Name:  cr-10
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***   Single Operator Precision    ***
----------------------------------------
Analyte:  Cr          Matrix:  Acid Mine Drainage
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):     2.5972
          Slope (b):      .0561
    =============================
                                           Single
           Sample Weights                Operator   Estimated
    Pair   Size       (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      13     86.18      4.6978      2.8672      2.8606
      2      13     12.05     60.3978      6.1214      5.9844
      3      14      1.29    255.1978     14.1162     16.9091
      4      14       .39    489.1978     32.7816     30.0323
      5      13       .10    956.6978     59.3823     56.2505
    -----------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    =========================================================
      a:     4.8491      Intercept (a'):     1.5788
      b:     1.0030          Slope (b'):      .0030
    =========================================================
                                                  Single
           Sample Weight               Operator   Estimated
    Pair   Size      (%)        Conc     Std Dev     Std Dev
    ---------------------------------------------------------
      1      13    19.34      4.6978      2.8672      4.9174
      2      13    19.34      4.6978      6.1214      5.8041
      3      14    20.99     50.5978     14.1162     10.3647
      4      14    20.99     70.1978     32.7816     20.7995
      5      13    19.34    220.1978     59.3823     83.6366
    ---------------------------------------------------------

File Name:  cr-10
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***       Overall Precision        ***
----------------------------------------
Analyte:  Cr          Matrix:  Acid Mine Drainage
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Overall Precision ***

    - Linear Model - s = b*T + a
    =============================
      Intercept (a):     4.1036
          Slope (b):      .1031
    =============================
    Conc   Sample   Weights                Overall   Estimated
    Level  Size         (%)        Conc     Std Dev     Std Dev
    -------------------------------------------------------------
      1      13       24.55      4.6978      3.7863      4.5878
      2      14       26.64      4.6978      6.3133      4.5878
      3      14       19.74     50.5978      8.6095      9.3182
      4      13       16.01     70.1978     10.3938     11.3381
      5      14        6.52    220.1978     29.1820     26.7969
      6      14        4.13    290.1978     30.7591     34.0110
      7      14        1.39    457.1978     55.0168     51.2218
      8      14         .91    521.1978     47.0603     57.8176
      9      14         .07    912.1978    165.5899     98.1135
     10      13         .04   1001.1980    119.7204    107.2857
    -------------------------------------------------------------


    - Curvilinear Model - s = a*(b**T)  ( ln s = b'*T + a')
    ===========================================================
      a:     7.9953      Intercept (a'):     2.0788
      b:     1.0033          Slope (b'):      .0033
    ===========================================================
    Conc   Sample   Weight                Overall   Estimated
    Level  Size        (%)        Conc     Std Dev     Std Dev
    -----------------------------------------------------------
      1      13        9.44      4.6978      3.7863      8.1189
      2      14       10.24      4.6978      6.3133      8.1189
      3      14       10.24     50.5978      8.6095      9.4316
      4      13        9.44     70.1978     10.3938     10.0550
      5      14       10.24    220.1978     29.1820     16.4095
      6      14       10.24    290.1978     30.7591     20.6235
      7      14       10.24    457.1978     55.0168     35.5783
      8      14       10.24    521.1978     47.0603     43.8473
      9      14       10.24    912.1978    165.5899    157.1880
     10      13        9.44   1001.1980    119.7204    210.1988
    -----------------------------------------------------------
```

```
File Name:  cr-10
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ************  Recovery  **************
----------------------------------------
Analyte:  Cr          Matrix:  Acid Mine Drainage
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Recovery ***

    - Linear Model - X = b*T + a
    =============================
      Intercept (a):      .2353
          Slope (b):      .9225
    =============================
    Conc   Sample   Weights                  Mean   Estimated
    Level  Size         (%)      Conc      Result      Result
    ----------------------------------------------------------
      1      13     38.87      4.6978      4.5862      4.5689
      2      14     41.86      4.6978      4.8014      4.5689
      3      14     10.15     50.5978     44.6071     46.9113
      4      13      6.36     70.1978     66.5308     64.9922
      5      14      1.23    220.1978    205.5072    203.3660
      6      14       .76    290.1978    267.9786    267.9405
      7      14       .34    457.1978    429.1429    421.9967
      8      14       .26    521.1978    476.5000    481.0362
      9      14       .09    912.1978    834.4286    841.7307
     10      13       .07   1001.1980    923.7692    923.8325
    ----------------------------------------------------------
```

```
File Name:  cr-10
Statistical Analysis File (.STT)


----------------------------------------
 *** Performance Estimation Results ***
 ***     Precision vs Recovery      ***
----------------------------------------
Analyte:  Cr          Matrix:  Acid Mine Drainage
Project:  AMQ-TC      Method:  GFAAS
   Date:  12/13/1995
  Units:  ug/L

 *** Single Operator Precision vs Recovery ***
           (Obtained by Substitution)

     - Linear Model - s = f*X + e
    ==============================
        Intercept (e):     2.3421
            Slope (f):      .0608
    ==============================


     - Curvilinear Model - s = e*(f**X)
    ====================================
        Intercept (e):     4.8454
                  (f):     1.0032
    ====================================



 *** Overall Precision vs Recovery ***
       (Obtained by Substitution)

     - Linear Model - s = f*X + e
     =============================
        Intercept (e):     3.8486
            Slope (f):      .1117
     =============================


     - Curvilinear Model - s = e*(f**X)
     ===================================
        Intercept (e):     7.9886
                  (f):     1.0035
     ===================================
```