

STUDY PLAN

Evaluation of Statistical Approaches to Developing Detection and Quantitation Limits

1.0 Introduction

Over the past decade, academicians, members of the regulated industry, and others, have developed various statistical approaches to detection limits and quantitation limits. For the most part, these approaches have been based on very limited data. A concern is that any statistical model based on limited data will be indicative of that data only, and may not be applicable to a broader range of analytical data. Characterization of the signals from various instruments would therefore be desirable. This study plan gives details of characterization of signals from an ICP/MS instrument.

Inductively coupled plasma/mass spectrometry (ICP/MS) is used for determination of antimony, cadmium, copper, lead, nickel, selenium, silver, thallium, and zinc using EPA Methods 200.8 and 1638. (Note: Method 1638 is a more recent revision of 200.8 that incorporates clean techniques to achieve lower method detection limits.) Method detection limits (MDLs) have been determined for these elements using Method 200.8 and Method 1638, and minimum levels (MLs) have been established using Method 1638.

2.0 Objective

The objective of this study is to collect data for antimony, cadmium, copper, lead, nickel, selenium, silver, thallium, and zinc using EPA Method 1638, and to use these data to establish detection and quantitation limits using the various statistical approaches listed in Table 1.

Detailed study objectives are to:

- use the data collected in this study to populate the statistical models and thereby more fully evaluate the various statistical approaches.
- characterize the signals from the ICP/MS instrument for nine elements from near the upper end of the linear range to extinction on the lower end, using EPA Method 1638.
- determine, at a given true concentration, the nature of the distribution of measurements given the analytical system being studied (sample preparation and instrumental analysis).
- determine the shape of the error vs concentration curve over the range of concentrations measured.

In order to meet these objectives, and to ensure that the data produced are of the highest possible quality, the laboratory will be required to have a comprehensive QA program in place and operating throughout the duration of this study. The laboratory will be required to follow all QC

procedures defined in this study plan and in EPA Method 1638 with the following exceptions:

- Demonstration of initial precision and recovery (IPR) and ongoing precision and recovery (OPR) will not be required.
- Performance of matrix spike, matrix spike duplicate, or duplicate analyses (laboratory fortified sample matrix or laboratory duplicates) will not be required.
- Sample digestion will not be required. However, it may be necessary to add a small amount of acid to the samples to assure that the elements remain in solution and to match the acid concentration with that of the solutions used for calibration.

If the procedures described in this Study Plan conflict with those described in Method 1638, the Study Plan will take precedence.

3.0 Study Management/Limitations

This study will be managed by the Office of Water's Engineering and Analysis Division through the Analytical Methods Staff (AMS). Day-to-day management and coordination of study activities will be provided by the contractor-operated Sample Control Center (SCC) under AMS guidance. SCC will contract a laboratory experienced with the determination of dissolved elements at EPA water quality criteria (WQC) levels using inductively coupled plasma-mass spectrometry (ICP-MS). SCC will then coordinate laboratory analysis, receive and validate all analytical data, and perform statistical analyses. Changes or deviations from this Study Plan must have prior approval from SCC. AMS will draw conclusions from the results, and produce a report providing the results of the study. Upon request, AMS will share data and results with all interested parties.

All correspondence should be communicated to Michelle Gallice at (703) 519-1213 or by facsimile at (703) 684-0610. All data from this study will be submitted to SCC for review and validation and should be sent to:

DynCorp
Sample Control Center
300 North Lee Street
Alexandria, VA
Attn: Michelle L. Gallice

4.0 Technical Approach/Limitations/Procedures

4.1 Contamination

A concern in making trace metal determinations is the effect of contamination on the measurement. For the tests described in this Study Plan, it is desirable that the level of contamination from any element be at least an order of magnitude (factor of 10) below the lowest level measured. If not, it will be necessary to characterize the level of contamination and perform blank-subtraction in order to produce reliable measurements. However, the level at which reliable blank-subtraction can be performed is limited by the precision of measurements, and the precision becomes progressively worse at lower

measurement levels. It is a requirement of this study that all data must be associated with uncontaminated blanks. Reagent water to be used for blanks shall be prepared using filtration, ion exchange, reverse osmosis, or any other technique necessary to assure that the measurements in this study are not compromised by contamination from this source.

4.2 Sample Preparation

4.2.1 Prepare stock and spiking solutions of the elements listed in Method 1638 such that the maximum concentration of each element will be near the upper end of the linear range of the ICP/MS instrument. It is anticipated that this concentration will be 100 ug/L. Using the spiking solution(s), prepare dilutions at concentrations of 100, 50, 20, 10, 5, 2, 1, 0.5, 0.2, 0.1 ug/L, and to lower concentrations if it is anticipated that a lower concentration will be detected for any element. The laboratory may adjust these dilution levels based on historical data and best professional judgement with prior approval by SCC.

4.2.2 The concentration of acid in all samples, standards, and blanks should be maintained constant to preclude variability from this source.

4.3 Instrument Optimization

It is desirable that measurements in this study be made at as low a level as possible. Therefore, it is a requirement of this study that all data must be made on an ICP/MS instrument that is operated to achieve maximum sensitivity. All runs must be done by a single operator on a single machine; and samples should be run from the highest concentration to the lowest concentration. In addition, the use of an ultrasonic nebulizer for sample introduction is required to ensure the study MDL objectives are met.

All specifications for calibration (CAL) and calibration verification (VER) in Method 1638 shall be met.

4.4 Analysis

Calibrate the instrument per Method 1638 using the internal standard method.

Using the solutions prepared in Section 4.2 of the Study Plan, analyze seven (7) replicates of each solution at each level, beginning with the most concentrated solution and working downward until a minimum of three of the seven replicates show no signal or no increase in signal above the blank level. Rinse the analytical system between each measurement and each level to assure no carryover between measurements and levels. At the end of the sequence, analyze seven replicate blanks.

Verify calibration after measurements at two successive levels, matching the concentration of the verification solution to one of the level being measured.

5.0 Reporting Requirements

Place the results in a spreadsheet and transmit the spreadsheet via diskette and hardcopy to the

Sample Control Center. If more than one m/z is used for determination of an element, report results for each m/z. Report results for all analytes and internal standards.

Submit all hardcopy raw data (instrument output, prep logs, etc.) required to reconstruct the results that are reported in the spreadsheet described above.

The laboratory shall not perform any data censoring or obscure any data by using data qualifiers such as "ND" or artificial zeros. The analyses should be performed exactly once without any reruns, or if there is a technical problem all seven (7) analyses should be rerun.

6.0 Statistical Analysis

For each analyte, SCC will calculate the detection and quantitation limits according to each concept, and will then compare results.

Data from this study will be used to populate the detection and quantitation limit models listed in Table 1 to evaluate the results achieved with the various models.

The statistical premises of each DL/QL concept will be statistically tested against the data for each analyte. Where appropriate, parametric models for the error versus concentration curve will be fitted and evaluated for goodness of fit to the data.

Table 1
Detection and Quantitation Limit Concepts

Organization/Author	Statistical Model ¹	Detection Limit		Quantitation Limit	
		Term	Sigma ²	Term	Sigma ²
ACS/Keith	Currie	LOD	3	LOQ	10
APHA/AWWA/WEF	Currie	MDL	6.4	LOQ	16
ASTM/Coleman	Hubaux/Vos	IDE	10 est	-----	-----
Caulcutt/Boddy	Currie	COD	1.9	LOD	4.8
DOE	Currie	IDL	3.0	-----	-----
DOE/Karnofsky	Currie	MDA	4.8	-----	-----
EPA AREAL	Currie	LOD	3.0	-----	-----
EPA ESID/Sinha	Hubaux/Vos	MDL	varied	-----	-----
EPA NERL	Currie	MDL	3.1	-----	-----
EPA OERR	Currie	-----	-----	CRQL	vote
EPA OGWDW	Currie	MDL	3.1	PQL	16-32
EPA OST	Currie	MDL	3.1	ML	10
EPA OSW	Currie	MDL	3.1	EQL	16-32
Hunt/Wilson	Currie	LOD	4.7	LLDr	10
IIAG/Koorse 1993	Currie	CMDL	-----	CMQL	45 est
IIAG/Koorse 1995	Hubaux/Vos	-----	-----	AML	40 est
IUPAC 1975	Currie	LOD	3	LOQ	10
IUPAC/Currie 1995	Currie	MDV	3.3	QL	10
NOAA	Currie	LOD	3	-----	-----
USATHAMA	Hubaux/Vos	-----	-----	CRL	8 est

1 The Currie model uses a multiple of the standard deviation to establish the detection and/or quantitation limit; the Hubaux/Vos model uses the calibration function to establish these limits.

2 Sigma refers to the multiple of the standard deviation used or estimated to establish the detection/quantitation limit, and can be used for comparison purposes.

Detection and Quantitation Limit Term Definitions

LOD	=	Limit of detection
LOQ	=	Limit of quantitation
MDL	=	Method detection limit
COD	=	Criteria of Detection
IDL	=	Instrument detection limit
MDA	=	Minimum detectable amount
CRQL	=	Contract required quantitation limit
PQL	=	Practical quantitation level
ML	=	Minimum level
EQL	=	Estimated quantitation level
LLDr	=	Lower limit of determination
CMDL	=	Compliance monitoring detection level
CMQL	=	Compliance monitoring quantitation level
AML	=	Alternate minimum level
MDV	=	Minimum detectable value
QL	=	Quantitation level
CRL	=	Certified reporting level